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PROCEEDINGS OF THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

Spectrometric Determinations of the Effect of a Neutral Salt on the Dissociation of Acetic Acid.

By N. V. SIDGWICK, F.R.S., and L. A. WOODWARD.

(Received July 30, 1930.)

This paper gives an account of an extension of the work contained in the preceding paper (Sidgwick, Worboys and Woodward). For the first part the simple photoelectric colorimeter described in that paper was used. For the second part a new type of flicker photometer was constructed. The principle of both instruments is the same, and has been given in the previous paper together with the theory of the colour changes of methyl orange, the indicator used throughout.

The colour measurements allow us to determine the value of the apparent dissociation constant K of methyl orange in presence of various concentrations of neutral salt. At a given salt concentration therefore the use of the appropriate K value will enable us to calculate the true hydrogen ion concentration of such a solution from its colour. In this way the degree of dissociation of acetic acid has been investigated in presence of different amounts of the neutral salt potassium bromide.

PART I.—PRELIMINARY MEASUREMENTS WITH THE SIMPLE PHOTOMETER.

Determination of the Dissociation Constant of Acetic Acid in Absence of Neutral Salt.

The solutions used contained N/40,000 methyl orange and N/500 sodium acetate, together with a range of concentrations of acetic acid. At N/500 the sodium acetate represses the ionisation of the acetic acid considerably, but its neutral salt effect on the activity coefficients of the substances present must be negligibly small.

The acetic acid was purified as described by Bousfield and Lowry,* by repeated distillation from potassium permanganate with an efficient still-head. The purity of the product and its freedom from formic acid were tested by determination of the maximum conductivity in water. The sodium acetate was the purest available B.D.H. trihydrate; it was recrystallised from water with the aid of a centrifuge, and then carefully dehydrated below 120° .† In preparing the solutions conductivity water was always used, and the precautions of the previous paper were observed.

The wave-length of the spectrum band used was selected, as before, so as to give values of c_1 (the ratio of the acid to the alkaline colour) lying between 2.5 and 3.0. Three sets of measurements were made, each with a series of acid concentrations. The value of c_1 was determined separately for each set; its small variations, due to a slight difference in the setting of the apparatus, do not affect the validity of the results. The temperature was $18^{\circ} \pm 1^{\circ}$. The results are given in Table I. The first column contains the total concentration of acetic acid; the second the observed relative colour (as defined in the previous paper); the third the values of $[H_{free}]$ calculated from the equation

$$[H_{free}] = K \cdot \frac{(c - 1)}{(c_1 - c)}.$$

The value of K used was 3.0×10^{-4} , as determined at 18° with this apparatus. The fourth gives the concentration of hydrogen ions combined with indicator anions, according to the equation

$$[H_{bound}] = \frac{c - 1}{c_1 - 1} \cdot \frac{1}{40,000}.$$

The acetanion concentrations $[A]$ in the fifth column are obtained by the relation

$$[A] = [H_{bound}] + [H_{free}] + [NaA],$$

assuming complete ionisation of the sodium acetate at $N/500$. The concentrations of the undissociated acetic acid, $[HA]$ of the sixth column, are given by

$$[HA] = [\text{total acetic acid}] - [H].$$

The values of K_{HA} (last column) are calculated from the ordinary mass-action equation

$$K_{HA} = \frac{[H_{free}] \cdot [A]}{[HA]}.$$

* 'J. Chem. Soc.,' vol. 99, p. 1432 (1911).

† See Green, 'J. Phys. Chem.,' vol. 12, p. 655 (1908).

Table I.—Acetic Acid + N/500 Sodium Acetate.

	[Acetic acid] $\times 10^4$.	c obs.	[H _{free}] $\times 10^4$.	[H _{bound}] $\times 10^4$.	[A] $\times 10^4$.	[HA] $\times 10^4$.	K _{HA} $\times 10^4$.
Set 1. $c_1 = 2.90$	1327	2.45	8.53	0.18	28.71	1318	1.86
	925.5	2.34	6.48	0.17	26.65	898.9	1.92
	617.0	2.19	4.63	0.15	24.78	592.2	1.94
	462.7	2.04	3.39	0.13	23.52	439.2	1.81
	370.2	1.94	2.76	0.12	22.88	347.3	1.82
Set 2. $c_1 = 2.85$	1234	2.34	7.88	0.18	28.06	1226	1.81
	740.4	2.17	5.16	0.16	25.32	735.1	1.78
	370.2	1.89	2.78	0.12	22.90	367.3	1.73
	185.1	1.61	1.48	0.08	21.56	183.5	1.74
Set 3. $c_1 = 2.62$	1481	2.23	9.30	0.19	29.49	1472	1.86
	1111	2.15	7.33	0.18	27.52	1103	1.83
	789.8	2.06	5.68	0.16	25.84	784.0	1.87
	493.6	1.90	3.75	0.14	23.89	489.7	1.83
	296.2	1.71	2.33	0.11	22.44	293.8	1.78

They are satisfactorily constant, and the mean value 1.83×10^{-5} at 18° is in complete agreement with the accepted value from conductivity measurements.

It is to be noted that the form of the mathematical relationships involved is such as to magnify experimental errors. The sodium acetate diminishes this, providing a large and constant amount of acetanions, which makes the percentage variation of [A] due to an error in colour measurement small. Slight variations in temperature will have a considerable effect, owing to the large temperature coefficient of the indicator K.

Effect of 2N Potassium Bromide on the Colour of Methyl Orange.

It had been found (previous paper) that the absorption of the yellow and red forms of methyl orange was slightly increased by the presence of neutral salts, but to the same extent, so that the value of c_1 was unaltered. This effect was remeasured with slightly different results, which were shown, however, not to affect the conclusions. Solutions of methyl orange (N/40,000) were used, one being slightly alkaline (100 per cent. yellow form) and the other having an excess of hydrochloric acid (100 per cent. red form). The absorptions were measured in absence and presence of 2N potassium bromide. The salt was recrystallised from water with the aid of a centrifuge. It was found that the absorption of the yellow (alkaline) form was increased by about 10 per cent., and that of the red (acid) form only by about 1 per cent., so that c_1 is somewhat

decreased by the presence of the salt. In one experiment, for example, a mean value of $c_1 = 2.89$ in absence of salt fell to 2.65 in presence of 2N KBr.

To discover whether this discrepancy affected the results, we redetermined the apparent dissociation constant of methyl orange in presence of 2N KBr, for comparison with the value given in the previous paper. In the previous measurement a range of concentrations of salt and only one of acid were used; we therefore now used a range of acid strengths and only one of salt. This further served to test the dependence of the neutral salt effect upon the hydrogen ion concentration.

The solutions contained N/40,000 methyl orange and 2N potassium bromide. The measurements were made as before; temperature 18°. Two sets were made, and the results are given in Table II.

Table II.—Hydrochloric Acid and 2N Potassium Bromide.

	$[\text{HCl}_{\text{total}}] \times 10^4$	c observed.	$[\text{H}_{\text{bound}}] \times 10^4$	$[\text{H}_{\text{free}}] \times 10^4$	$K \times 10^4$
Set 1. $c_1 = 2.59$	3.82	2.25	0.20	3.62	0.98
	2.12	2.06	0.17	1.95	0.97
	1.70	1.99	0.16	1.54	0.93
	1.27	1.89	0.14	1.13	0.89
	0.848	1.72	0.113	0.735	0.89
Set 2. $c_1 = 2.695$	3.82	2.35	0.20	3.62	0.93
	2.76	2.25	0.18	2.58	0.92
	1.91	2.12	0.17	1.74	0.89
	1.48	2.00	0.15	1.33	0.93
	1.06	1.84	0.12	0.94	0.96

The values in the third, fourth, and fifth columns are obtained from the relations

$$[\text{H}_{\text{bound}}] = \frac{c - 1}{c_1 - 1} \cdot \frac{1}{40,000},$$

$$[\text{H}_{\text{free}}] = [\text{HCl}_{\text{total}}] - [\text{H}_{\text{bound}}],$$

$$K = [\text{H}_{\text{free}}] \cdot \frac{c_1 - c}{c - 1}.$$

An error of 1 per cent. in observed colour will cause errors in K of 4 per cent. in the lowest and 8 per cent. in the highest acid concentrations. The values of K obtained are reasonably constant, and the mean value, 0.93×10^{-4} at 18°, in 2N potassium bromide, is not seriously different from that (0.99×10^{-4}) given in the previous paper.

Determination of K_{HA} in Presence of Neutral Salt.

This value, 0.93×10^{-4} of K for methyl orange in 2N KBr, was used to investigate the dissociation of acetic acid under the same conditions. The solutions contained N/40,000 methyl orange, 2N KBr, and N/500 sodium acetate. As mentioned above, the sodium acetate has a negligible neutral salt effect, but increases the accuracy of the deductions by giving an excess of acetanions. The results are given in Table III, which is analogous to Table I.

Table III.—HA + N/500 NaA + 2N KBr.

	[Acetic acid] $\times 10^4$.	c obs.	[H _{free}] $\times 10^4$.	[H _{bound}] $\times 10^4$.	[A] $\times 10^4$.	[HA] $\times 10^4$.	K_{HA} $\times 10^4$.
Set 1. $c_1 = 2.695$	388.7	2.30	3.06	0.19	23.25	385.5	1.85
	259.1	2.18	2.13	0.17	22.40	256.7	1.85
	172.8	2.035	1.46	0.15	21.61	171.2	1.84
	129.5	1.93	1.13	0.14	21.27	128.2	1.88
	86.38	1.77	0.775	0.113	20.89	85.49	1.90
Set 2. $c_1 = 2.68$	518.2	2.37	4.11	0.20	24.31	513.9	1.94
	388.7	2.31	3.29	0.20	23.49	385.2	2.00
	276.4	2.21	2.40	0.18	22.58	273.2	1.98
	215.9	2.13	1.92	0.17	22.09	213.8	1.98
	155.5	2.01	1.40	0.15	21.55	154.0	1.96

The mean value of K_{HA} at 18° is 1.92×10^{-5} , as compared with 1.83×10^{-5} in absence of neutral salt, so that the salt causes an increase of only about 5 per cent. Recent work on the variation of activity coefficient with ionic strength would, however, lead us to expect that the neutral salt effect would be in general much larger than this, and that the dissociation would increase at low salt concentrations, pass through a maximum, and then decrease. Thus at a certain concentration for each salt the effect must be zero; and it was thought that the small change observed in K_{HA} in 2N KBr was due to an accidental choice of a salt concentration near this point. We therefore decided to examine a range of salt concentrations, and for this purpose constructed the flicker photometer described in the next section.

PART II.—THE FLICKER PHOTOMETER.

The principle of this apparatus is the same as that of the simple photometer described in the previous paper, but it is far more accurate and convenient to use. In its construction we have had the advantage of the continual assistance and advice of Dr. G. M. B. Dobson, to whom we are very grateful.

By means of a suitable optical arrangement (described below) a beam of monochromatic light of known wave-length can be made to enter the same photoelectric cell by one or other of two routes, either through the compartment in which the cell containing the solution under investigation may be placed, or through an optical wedge. The colour of a given solution is then obtained as follows. Before introducing the cell with the solution, the photoelectric effect of the beam after passing through the empty chamber is noted. The beam is then deflected so as to pass through the wedge, and the wedge position corresponding to the same photoelectric effect as before is observed. This may be called the "zero position." Then the absorption cell with the coloured solution is placed in the chamber and the light sent normally through it. The electrometer reading is observed, and the beam deflected through the wedge, which is then shifted so as to give the same reading. As shown in the previous paper the lateral shift of the optical wedge from its "zero position" gives a direct measure of the absorption of the solution together with the cell containing it.

Thus each colour measurement involves the observation of two wedge positions, each of which involves the balancing by a null-point method of two photoelectric effects which are produced by the beam after travelling respectively two different paths. It is essential for accuracy that the change over from one path to the other should be as rapid as possible, and accompanied at the null-point by the minimum transient diminution of the intensity of light, *i.e.*, the minimum flicker of the electrometer needle. With our apparatus it is possible, when the wedge is correctly adjusted, to change over rapidly from one light path to the other with no observable flicker.

A diagrammatical representation of the apparatus is shown (only roughly to scale) in fig. 1. The source of light L is a 500-watt, gas-filled filament lamp, mounted to allow of focusing and lit directly from the laboratory mains. Owing to the heat generated this must be surrounded by a double-walled metallic jacket J through which water circulates. The light is focused on the slit of a Tutton monochromator by Hilger, a constant deviation instrument in which the wave-length can be read off directly from the drum which moves the prism (M). The monochromatic beam is made parallel by the lens S. The arrangement for changing the path of the beam consists of two totally reflecting prisms, P_1 , P_2 , carried on a horizontal metal table which can be moved vertically by hand. When the table is depressed, the beam passes over the top of the prism P_1 , through the absorption chamber A, and is focused on the photoelectric cell C. When the table is raised, the beam suffers total reflection at P_1 , passes

normally through the optical wedge *W*, is reflected at *P*₂, and finally focused again upon *C*. While it is being raised or depressed, part of the light goes one

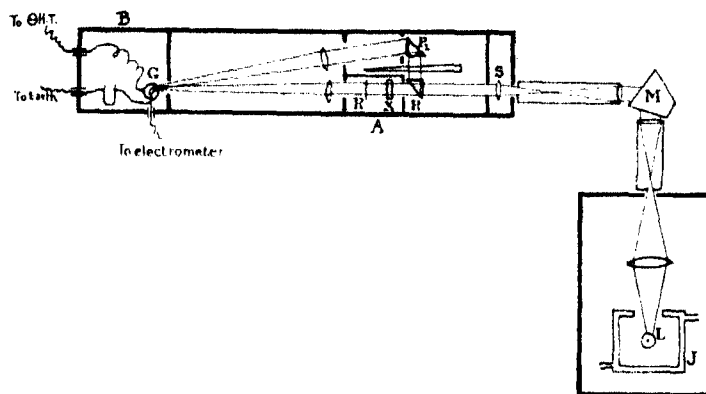


FIG. 1.—Apparatus (roughly to scale of 1/20th inch = 1 inch).

way and part the other; thus no "flicker" is produced in the photoelectric effect if the wedge is correctly adjusted at the null-point. Owing to the loss of intensity in passing through the prisms, it is necessary to insert an absorbing screen *R* of suitable density in the absorbing chamber; otherwise the "zero position" cannot be realised. The optical wedge is held by an arm attached to a brass carriage running accurately on parallel steel bars. The carriage position can be set roughly by hand, and final adjustment is by a micrometer movement, the position being read off on a vernier scale. The solution to be investigated is contained in the rectangular glass cell *X*, the liquid layer being 1 cm. thick, and the whole cell holding only about 6 c.c. The electrical connections to the photoelectric cell *C* are similar to those described in the previous paper, the xylene leak, two-way switch, etc., being all contained along with *C* in a compartment *B*, which is completely lined with earthed copper sheet. The current is measured as before with a Lindemann-Keeley electrometer. The whole apparatus is carried on a single base of multiple-ply wood to avoid warping, and, with the exception of the monochromator, all is contained in two mahogany boxes fitted with levelling screws.

The apparatus can be made practically light-tight, and so need not be used in a dark room. The accuracy of the results is not affected by variations in the light source or in the photoelectric apparatus, etc., if these are sufficiently slow not to be mistaken for genuine "flickers" of the needle. In practice no difficulty is found in obtaining good null-points.

For experiments with methyl orange it is desirable to control the temperature.

To this end the cell with the solution (protected by a cover-slip) was placed for some time in an air-bath kept at 18° by immersion in the water of a thermostat at a slightly higher temperature. It was then transferred to the absorption chamber, the temperature of which was regulated by blowing into it a stream of air previously heated by passage over an electrically heated resistance wire. By suitable hand regulation the chamber could be kept at $18^{\circ} \pm 0.2^{\circ}$, and the solution during measurement was well between these limits.

PART III.—MEASUREMENTS WITH THE FLICKER PHOTOMETER.

Test of the Colour Theory for Methyl Orange over the Range of the Optical Spectrum.

It had been found in the previous work that satisfactory results could be obtained by using only a certain empirically selected range of wave-lengths. The present measurements were undertaken in order to test the applicability of the Tizard equation at other wave-lengths.

Five solutions were made up, each containing N/40,000 methyl orange. One was made slightly alkaline (2 drops of N potassium hydroxide to 100 c.c.), and one contained N/10 hydrochloric acid; the other three contained intermediate concentrations of this acid. The absorptions were measured at 18° for a series of 10 wave-lengths from 4500 to 5625 Å.U., a rubidium photo-electric cell being used. Every measurement was repeated at least twice with fresh solutions, and the agreement was satisfactory. The mean results are given in Table IV.

Table IV.—Methyl Orange + Hydrochloric Acid.

λ in Å.U.	D obs.	I. obs.	Acid I.		Acid II.		Acid III.	
			X obs.	Per cent. red.	X obs.	Per cent. red.	X obs.	Per cent. red.
5625	2.66	0.66	2.27	(80.5)	2.06	(70.0)	1.62	(48.0)
5500	6.25	0.88	5.10	78.6	4.56	68.5	3.42	47.3
5375	9.95	1.39	8.11	78.5	7.30	69.0	5.33	46.0
5250	11.37	2.20	9.46	79.2	8.54	69.1	6.44	46.2
5125	12.07	3.40	10.26	79.1	9.37	68.9	7.36	45.9
5000	12.02	4.64	10.47	79.0	9.76	69.4	8.06	46.3
4875	10.63	5.97	9.60	77.9	9.10	67.2	8.10	45.7
4750	8.23	6.82	7.96	(80.8)	7.76	(66.7)	7.49	(47.5)
4625	5.84	6.94	6.15	(71.8)	6.23	(64.6)	6.52	(39.7)
4500	4.03	6.57	4.59	78.0	4.86	67.3	5.43	46.4
			Mean	78.6	Mean	68.5	Mean	46.3

The first column gives the wave-lengths in A.U. ; the second and third the observed wedge shifts in centimetres for the excess acid solution (D) and the slightly alkaline solution (L). The rest of the table gives for each of the three intermediate acid concentrations X, the observed wedge shift, and the percentage of the red form present. These shifts are not corrected for the absorption of the glass cell and the water ; this correction is constant throughout, and since in the calculations we deal only with the differences of wedge shifts, it vanishes. In the previous treatment of results use has been made of relative colours, but the results with the flicker apparatus will always be given in terms of observed wedge shifts. The following relations hold :

$$c = (X - w)/(L - w) \quad \text{and} \quad c_1 = (D - w)/(L - w),$$

where w = absorption of cell + water. The Tizard equation (equation (3), previous paper) becomes

$$K = [H] \cdot (D - X)/(X - L),$$

which is seen to be independent of w .

The percentage of indicator present in the red form at each acid concentration is calculated according to Tizard's additive law from the equation

$$\text{Percentage red} = (X - L)/(D - L).$$

With the exception of certain bracketed values (see below) concordant results are obtained over the whole spectrum.

The results are shown graphically in fig. 2, in which observed wedge shifts are plotted against wave-lengths. The curves for the excess acid solution (100 per cent. red) and for the alkaline solution (100 per cent. yellow) intersect at about $\lambda = 4685$ A.U. Since at this point the absorptions of the two forms are equal, any mixture of the two at the same total concentration should give the same value ; and this is proved by the fact that the curves for the three intermediate solutions all pass through this point.

In calculating the percentage of the red form present, the accuracy depends on the magnitude of the difference terms $(X - L)$ and $(D - L)$. When $\lambda = 4625, 4750$ and 5625 A.U. (the bracketed values in Table IV), the measurements cannot be expected to yield accurate results, in the first two because the absorptions of the two forms are so nearly equal, and in the last because the whole absorption is so small ; in reckoning the means these have been omitted.

The value of K for the indicator acid from the mean results in Table IV is given in Table V.

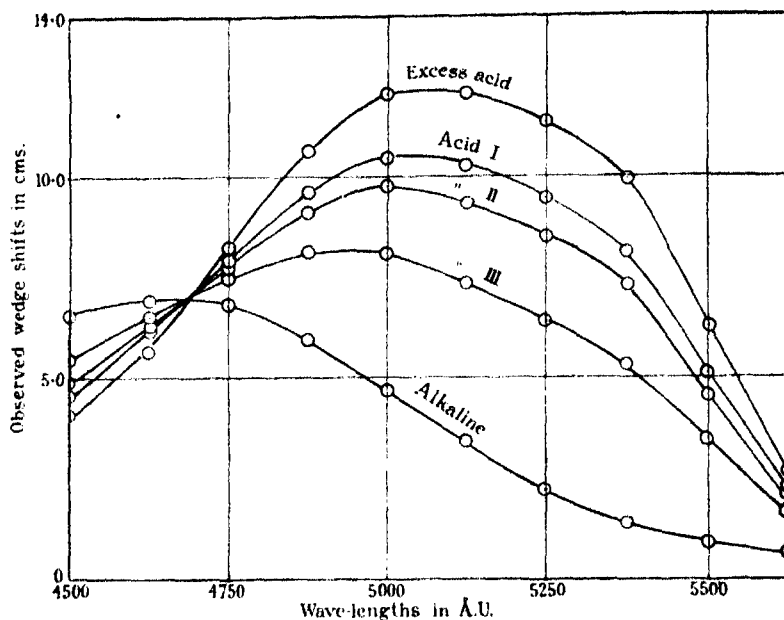


FIG. 2.

Table V.

Solution.	[HCl _{total}] × 10 ⁴ .	[H _{bound}] × 10 ⁴ .	[H _{free}] × 10 ⁴ .	K × 10 ⁴ .
Acid I	11.8	0.19	11.6	3.16
Acid II	7.39	0.17	7.22	3.32
Acid III	2.95	0.17	2.83	3.28

The third column is obtained from the relation

$$[\text{H}_{\text{bound}}] = \frac{X - L}{D - L} \cdot \frac{1}{40,000}$$

taking the mean values of the term $(X - L)/(D - L)$. The Tizard equation was used to calculate K, taking the mean values of $(D - X)/(X - L)$. The values of K show fair agreement, but point to a higher figure than that previously obtained (3.03×10^{-4}) with the simpler apparatus.

Determination of K for Methyl Orange at Optimum Wave-length.

The optimum wave-length is that showing the greatest difference of absorption between the two forms. For all subsequent measurements the wave-length 5125 Å.U. was selected, and a rubidium photoelectric cell, having its

maximum sensitivity in this region, was used. The temperature was regulated to $18^\circ \pm 0.2^\circ$, as described above. The indicator was N/40,000. The means of a number of concordant determinations are given in Table VI, which is similar to Table V.

Table VI.—Values of K for Methyl Orange at 18° .

$[\text{HCl}_{\text{total}}] \times 10^4$	X observed.	$[\text{H}_{\text{bound}}] \times 10^4$	$[\text{H}_{\text{free}}] \times 10^4$	$K \times 10^4$
7.03	9.11	0.17	6.86	3.42
6.03	8.79	0.16	5.87	3.41
4.74	8.39	0.15	4.59	3.25
4.06	8.00	0.13	3.93	3.34
3.29	7.56	0.12	3.17	3.30
2.22	6.70	0.10	2.12	3.31
Mean				3.34

The mean of a large number of determinations at this wave-length gave for the two forms the values $D = 11.98$ and $L = 3.32$ cm. Observational errors are magnified in the calculation of K; the figures in the last column of Table VI show that the error in the absorption measurements is always less than 1 per cent. The mean value of K, 3.34×10^{-4} , at 18° , is very near to that given by Güntelberg and Schiödt,* which is 3.23×10^{-4} at the same temperature.

Determination of K in Presence of Neutral Salt.

Analogous determinations were then made in presence of potassium bromide. It has already been shown (Table II) that the salt effect is independent of the acid concentration. For these experiments four concentrations of acid were used, and four of the salt, the latter being approximately N/10, N/2, N, and 2N. The materials were purified as before. Temperature $18^\circ \pm 0.2^\circ$, wave-length 5125 A.U. The results are given in Table VII, the mean of two independent concordant determinations being quoted in each case.

The table is in four parts, each of which is analogous to Table VI, and beside each are given the salt concentration and the mean observed values of D and L. For each part the appropriate values have been used in the calculation of K. The agreement of the calculated K-values at each salt concentration shows that the error in the absorption measurements is always less than 1 per cent. Since the value of K in absence of salt is 3.34×10^{-4} , it follows that with increasing salt concentration K passes through a maximum.

* 'Z. Phys. Chem.,' vol. 135, p. 393 (1928).

Table VII.—Methyl Orange + HCl + KBr.

	[HCl _{total}] × 10 ⁴ .	X observed.	[H _{bound}] × 10 ⁴ .	[H _{free}] × 10 ⁴ .	K × 10 ⁴ .	Mean K × 10 ⁴ .
[KBr] = 0.0916 N D = 12.03 L = 3.43	2.21	6.33	0.08	2.13	4.19	4.15
	3.29	7.14	0.11	3.18	4.19	
	4.06	7.60	0.12	3.94	4.19	
	4.74	8.02	0.13	4.61	4.03	
[KBr] = 0.458 N D = 12.08 L = 3.53	2.21	7.05	0.10	2.11	3.02	3.11
	3.29	7.87	0.13	3.16	3.07	
	4.06	8.28	0.14	3.92	3.14	
	4.74	8.55	0.15	4.59	3.21	
[KBr] = 0.916 N D = 12.12 L = 3.58	2.21	7.66	0.12	2.09	2.28	2.24
	3.29	8.57	0.15	3.14	2.23	
	4.06	9.00	0.16	3.90	2.25	
	4.74	9.35	0.17	4.57	2.19	
[KBr] = 1.832 N D = 12.31 L = 3.68	2.21	9.10	0.16	2.05	1.21	1.19
	3.29	9.89	0.18	3.11	1.21	
	4.06	10.30	0.19	3.87	1.17	
	4.74	10.52	0.20	4.53	1.18	

Determination of the Dissociation Constant of Acetic Acid in Absence of Neutral Salt.

This was done with N/40,000 methyl orange and pure acetic acid, but without sodium acetate. Temperature 18°, wave-length 5125 Å.U., D = 11.98, L = 3.32 cm. The results are given in Table VIII, which is analogous to Table I.

Table VIII.—Acetic Acid.

[Acetic acid] × 10 ⁴ .	X observed.	[H _{free}] × 10 ⁴ .	[H _{bound}] × 10 ⁴ .	[A] × 10 ⁴ .	[HA] × 10 ⁴ .	K _{HA} × 10 ⁵ .
999.3	10.28	13.7	0.20	13.9	975.4	1.95
582.6	9.84	10.19	0.19	10.38	572.2	1.85
272.4	9.18	6.99	0.17	7.16	265.2	1.89
124.7	8.36	4.65	0.145	4.795	119.9	1.86
101.6	8.06	4.04	0.14	4.18	97.4	1.73
72.69	7.74	3.48	0.13	3.61	69.08	1.82
61.95	7.53	3.16	0.12	3.28	58.68	1.77
50.58	7.37	2.93	0.12	3.05	47.53	1.88
33.98	6.90	2.35	0.10	2.45	31.53	1.83
25.13	6.66	2.10	0.09	2.19	23.12	1.99
Mean						1.86

The mean value, 1.86×10^{-5} , agrees with that found in the previous experiments (Table I: 1.83×10^{-5}).

Determination of K_{HA} in Presence of Potassium Bromide.

This was carried out in the same way as in the measurement of K (Table VII), with four concentrations of acetic acid, and four of potassium bromide (the latter the same as before). The same temperature and wave-length were used. The results are given in Table IX, which is arranged like Table VII.

Table IX.—Acetic Acid and Potassium Bromide.

	[Acetic acid] $\times 10^4$.	X obs.	[H _{free}] $\times 10^4$.	[H _{bound}] $\times 10^4$.	[A] $\times 10^4$.	[HA] $\times 10^4$.	K_{HA} $\times 10^4$.	Mean K_{HA} $\times 10^4$.
[KBr] = 0.0916 N D = 12.03 L = 3.43	33.98	6.94	2.86	0.10	2.96	31.02	2.73	2.74
	50.58	7.39	3.54	0.12	3.66	46.92	2.76	
	72.69	7.79	4.27	0.13	4.40	68.29	2.75	
	124.7	8.37	5.00	0.14	5.75	119.0	2.70	
[KBr] = 0.458 N D = 12.08 L = 3.53	33.98	7.69	2.95	0.12	3.07	30.91	2.93	2.86
	50.58	8.10	3.57	0.13	3.70	46.88	2.82	
	72.69	8.48	4.28	0.14	4.42	68.27	2.77	
	124.7	9.10	5.81	0.16	5.97	118.7	2.92	
[KBr] = 0.916 N D = 12.12 L = 3.58	33.98	8.24	2.69	0.14	2.83	31.15	2.44	2.48
	50.58	8.66	3.29	0.15	3.44	47.14	2.40	
	72.69	9.07	4.03	0.16	4.19	68.50	2.47	
	124.7	9.64	5.47	0.18	5.65	119.0	2.60	
[KBr] = 1.832 N D = 12.31 L = 3.68	33.98	9.44	2.39	0.17	2.56	31.42	1.94	1.89
	50.58	9.77	2.85	0.18	3.03	47.53	1.82	
	72.69	10.05	3.35	0.19	3.54	69.15	1.72	
	124.7	10.62	4.89	0.20	5.09	119.6	2.08	

For the calculation of $[H_{free}]$ by the Tizard equation, the proper value of the indicator K has been used at each salt concentration (i.e., the mean values from Table VII). The agreement in K_{HA} -values shows that the experimental error is always less than 1 per cent. The value of K_{HA} in absence of neutral salt being 1.86×10^{-5} these results show that with increasing salt concentration it passes through a maximum.

PART IV.—DISCUSSION OF RESULTS.

Comparison of Results from the Simple and Flicker Photometers.

The simple apparatus gave a value 3.0×10^{-4} of K for methyl orange at the room temperature of 18° , and this was used in the calculation of K_{HA} from the experiments in Part I of this paper, for which the same apparatus was employed. The new flicker colorimeter, however, has given the higher value 3.34×10^{-4} at a controlled temperature of 18° . This may be due, at least in

part, to the solutions in the earlier work not having attained the temperature of the room, since Tizard and Whiston have shown* that K for methyl orange increases by about 4 per cent. per degree. This explanation is supported by the fact that for the dissociation constant of acetic acid, which is little affected by temperature, both instruments have given practically the same values (1.83 and 1.86×10^{-5}), although the two different values of K were used in the two calculations. So, too, the values of K_a/K_c in presence of potassium bromide obtained by the simple apparatus (previous paper, Table IV) were, at salt concentrations of $0.5, 1.0, 2.0 \text{ N} : 1.06, 1.48, 3.06$; while interpolation from the values obtained with the new apparatus (this paper, Table VII) gives $1.10, 1.56, 3.12$. In general it seems that reliable results are obtained under given conditions if we use values of K determined under the same conditions. The recent determination of K for methyl orange by Güntelberg and Schiödt† is 3.23×10^{-4} at about 18° , which is in better agreement with our later value than with our earlier one, or with the value 3.0×10^{-4} got by interpolation from the earlier work of Tizard.‡

Theoretical Significance of Results.

The fundamental thermodynamic equation for a weak acid (see previous paper, equation (6)) is

$$K_a = \frac{a_H \cdot a_A}{a_{HA}} = \frac{f_H \cdot f_A}{f_{HA}} \cdot \frac{c_H \cdot c_A}{c_{HA}} = \frac{f_H \cdot f_A}{f_{HA}} \cdot K_c.$$

The results of the measurements with the flicker colorimeter are given in fig. 3. The acetic acid curve is got by plotting the values of $K_a/K_c = f_H \cdot f_A/f_{HA}$ against the square root of the volume normality of the potassium bromide (K_a is the value in absence of salt). We should expect the variation of f_A to be relatively small, and this has been approximately verified for acetic acid by the calculations of Randall and Failey,§ which are based on the experiments of Sugden|| upon partition between aqueous salt solutions and amyl alcohol at 25° . It is therefore interesting to compare the acetic acid curve with that for a strong acid, where the concentration of the undissociated part is zero. This is given in the HBr curve on fig. 3, which is taken from the electrometric

* 'J. Chem. Soc.,' vol. 117, p. 154 (1920).

† *Loc. cit.*

‡ 'J. Chem. Soc.,' vol. 117, p. 150 (1920).

§ 'Chem. Reviews,' vol. 4, p. 291 (1927).

|| 'J. Chem. Soc.,' vol. 129, p. 177 (1926).

results of Harned and James* for centinormal hydrobromic acid in potassium bromide solutions. Their units are slightly different from ours, but this does

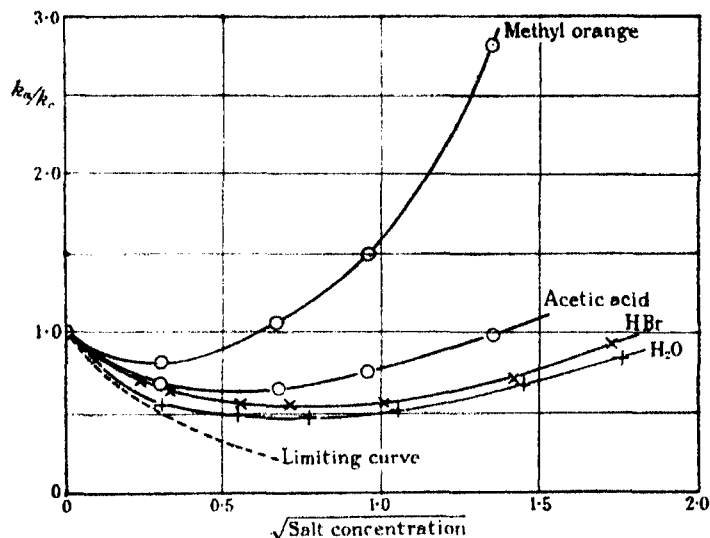


FIG. 3.

not affect the general shape of the curves (see previous paper). Their values for water ($\gamma_H \cdot \gamma_{OH}$ against the square root of the molality) are added; the lowest (dotted) curve gives the theoretical values for a uni-univalent electrolyte in dilute salt solutions according to the theory of Debye and Hückel (see previous paper).

It will be seen that all these curves, colorimetric and electrometric, are of the same form. In very dilute solutions all approximate to the theoretical limiting slope; each passes through a minimum at about the same salt concentration, and ultimately rises in concentrated salt solutions ($> 3N$) above its initial value. To the same class belong the later colorimetric measurements of Güntelberg and Schiödt (*loc. cit.*), and the approximate calculations of Harned† for formic acid, based on the rate of hydrolysis of methyl formate.

On the other hand, a sharp contrast is provided by the corresponding curve for methyl orange (K_a/K_c against the square root of the concentration: see Tables VI and VII). This shows a more marked deviation from the theoretical curve in very dilute solutions; the minimum occurs at a lower salt concentration (about 0.05 N); and the curve, after passing through the unit ordinate at a concentration of only about N/3, rises to much higher values in the strong

* 'J. Phys. Chem.,' vol. 30, p. 1060 (1926).

† 'J. Amer. Chem. Soc.,' vol. 49, p. 1 (1927).

solutions. The measurements of Güntelberg and Schiödt (*loc. cit.*, plotted in fig. 1 of the previous paper) confirm these conclusions. This difference must be due to the fact that with the indicator we have in addition to the equilibria ruling in a partly ionised solution of a weak electrolyte, another, the tautomeric equilibrium between the two structurally different forms. The more rapid rise of the curve for the indicator seems to show that this equilibrium is considerably shifted with increasing salt concentration towards the side of the non-dissociated (red) form.

We wish to express our thanks again to Dr. C. M. B. Dobson for his kind help, and also to Imperial Chemical Industries for a grant towards the cost of the work.

The Moments of the Distribution for Normal Samples of Measures of Departure from Normality.

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1. *The Appropriate Symmetric Functions of the Observations.*

If $x_1 \dots x_n$ are the values of a variate observed in a sample of n , from any population, we may evaluate a series of statistics (k) such that the mean value of k_p will be the p th cumulative moment function of the sampled population; the first three of these are defined by the equations:

$$\begin{aligned} k_1 &= \frac{1}{n} S(x), \\ k_2 &= \frac{1}{n-1} S(x - k_1)^2, \\ k_3 &= \frac{n}{(n-1)(n-2)} S(x - k_1)^3; \end{aligned}$$

then it has been shown (Fisher, 1929)* that the cumulative moment functions

* R. A. Fisher, "Moments and Product Moments of Sampling Distributions," 'Proc. Lond. Math. Society,' Series 2, vol. 30, pp. 199-238 (1929).

of the simultaneous distribution, in samples, of $k_1, k_2, k_3, \dots$, may be obtained by the direct application of a very simple combination procedure.

The simplest measure of departure from normality will then be

$$\gamma = k_3 k_2^{-3/2},$$

a quantity which is evidently independent of the units of measurement, and in samples from a symmetrical distribution will have a distribution symmetrical about the value zero. In testing the evidence provided by a sample, of departure from normality, the distribution of this quantity in normal samples is required.

Hitherto the exact values of the moments of this distribution have been unknown, though a method of calculating the moments for large samples, in a series of any number of powers of n^{-1} , has been given. It will be shown that the distribution may be investigated by means of a recurrence relation, which yields the moments of the distribution and seems well adapted for the investigation of its other properties.

2. The Recurrence Relation for γ .

For values of p from 1 to $n - 1$, let us define ξ_p by the relation

$$\xi_p = (x_p - k_1) + \frac{1}{n-1} (x_n - k_1),$$

or,

$$x - k_1 = \xi - \frac{1}{n-1} (x_n - k_1).$$

Then evidently

$$\sum_1^{n-1} (\xi_p) = 0$$

and

$$\sum_1^n (x_p - k_1)^2 = (x_n - k_1)^2 \left(1 + \frac{1}{n-1} \right) + \sum_1^{n-1} (\xi^2)$$

while

$$\sum_1^n (x_p - k_1)^3 = (x_n - k_1)^3 \left(1 - \frac{1}{(n-1)^2} \right) - \frac{3}{n-1} (x_n - k_1) \sum (\xi^2) + \sum (\xi^3),$$

so that, if

$$\frac{n}{n-1} (x_n - k_1)^2 = \cot^2 \theta \cdot \sum (\xi^2),$$

we may express the ratio

$$\gamma_n = \frac{n\sqrt{n-1}}{n-2} S (x - k_1)^3 \div S^{3/2} (x - k_1)^2$$

in terms of the ratio

$$\gamma_{n-1} = \frac{(n-1)\sqrt{n-2}}{n-3} S (\xi^3) \div S^{3/2} (\xi^2)$$

in the recurrence relation

$$\gamma_n = \frac{n(n-3)}{(n-1)^{1/2}(n-2)^{3/2}} \sin^3 \theta \cdot \gamma_{n-1} - \frac{3\sqrt{n}}{n-2} \cos \theta \sin^2 \theta + \sqrt{n} \cos^3 \theta, \quad (1)$$

where γ_{n-1} is the value of γ calculated from the sample values excluding x_n , and γ_n is the value calculated from the whole sample of n values.

The value of the recurrence relation in this form lies in the fact that the distribution of θ is independent of that of γ_{n-1} , for whatever may be the values of $\xi_1, \dots, \xi_{n-1} \div \sqrt{S(\xi^2)}$, if σ be the standard error of the population sampled the distribution of

$$t = (x_n - k_1) \sqrt{n/n-1}$$

will be

$$\frac{1}{\sigma \sqrt{2\pi}} e^{-t^2/2\sigma^2} dt;$$

hence if

$$c = t/\sqrt{2}$$

where S stands for $S(\xi^2)$, since the distribution of S is known to be

$$df = \frac{1}{(2\sigma^2)^{1/2(n-2)} \frac{n-4}{2}!} S^{1/2(n-4)} e^{-S/2\sigma^2} dS,$$

the distribution of c will be given by

$$df = \frac{dc}{\sigma \sqrt{2\pi}} \cdot \frac{(2\sigma^2)^{-1/2(n-2)}}{\frac{n-4}{2}!} \int_0^\infty e^{-\frac{S}{2\sigma^2}(1+c^2)} S^{1/2(n-3)} dS = \frac{\frac{n-3}{2}!}{\frac{n-4}{2}! \sqrt{\pi} (1+c^2)^{\frac{n-1}{2}}};$$

or, if c is $\cot \theta$, the distribution of θ is

$$df = \frac{\frac{n-3}{2}!}{\frac{n-4}{2}! \sqrt{\pi}} \sin^{n-3} \theta d\theta. \quad (2)$$

independently of the value of γ_{n-1} , as indeed is obvious if the sample is considered geometrically.

3. *The Distribution for Samples of 3.*

The terminal values of γ_n are given by putting $\theta = 0$ and π , when $\gamma_n = \pm \sqrt{n}$ irrespective of the values of γ_{n-1} which is indeed indeterminate at these values. The recurrence relation enables us also by means of a single integration to obtain the distribution of γ_n from that of γ_{n-1} , or alternatively to obtain the moments of the distribution of γ_n in terms of those of the distribution of γ_{n-1} . To utilise the recurrence relation in these ways we shall need the distribution of γ for the smallest possible samples, *i.e.*, for $n = 3$.

When $n = 3$, we may represent the 3 deviations of the observations from the mean of the population by

$$x_1 = b + a \cos \phi, \quad x_2 = b + a \cos \left(\phi + \frac{2\pi}{3} \right), \quad x_3 = b + a \cos \left(\phi + \frac{4\pi}{3} \right),$$

then the mean of the sample is b , and the statistics k_2 and k_3 are given by

$$\begin{aligned} k_2 &= \frac{a^2}{2} \left\{ \cos^2 \phi + \cos^2 \left(\phi + \frac{2\pi}{3} \right) + \cos^2 \left(\phi + \frac{4\pi}{3} \right) \right\} \\ &= \frac{3}{2} a^2 \\ k_3 &= \frac{3a^3}{2} \left\{ \cos^3 \phi + \cos^3 \left(\phi + \frac{2\pi}{3} \right) + \cos^3 \left(\phi + \frac{4\pi}{3} \right) \right\}, \end{aligned}$$

but

$$\cos^3 \phi = \frac{1}{4} (\cos 3\phi + 3 \cos \phi),$$

hence

$$k_3 = \frac{9}{8} a^3 \cos 3\phi,$$

and

$$\gamma \equiv k_3 k_2^{-3/2} = \sqrt{3} \cos 3\phi.$$

For the sampling distribution of ϕ , since

$$\frac{\partial (x_1, x_2, x_3)}{\partial (b, a, \phi)} = -\frac{3\sqrt{3}}{2} a,$$

and

$$x_1^2 + x_2^2 + x_3^2 = 3b^2 - \frac{3}{2} a^2,$$

we have

$$df = \frac{1}{(\sigma \sqrt{2\pi})^3} \cdot \frac{3\sqrt{3}}{2} \int_{-\infty}^{\infty} e^{-\frac{3b^2}{2\sigma^2}} db \int_0^{\infty} a e^{-\frac{3a^2}{4\sigma^2}} \cdot d\phi,$$

which on integration with respect to b yields

$$df = \frac{1}{(\sigma \sqrt{2\pi})^2} \int_0^{\infty} \frac{3a}{2} e^{-\frac{3a^2}{4\sigma^2}} da \cdot d\phi,$$

and on integration with respect to a , yields simply

$$df = \frac{1}{2\pi} d\phi.$$

Since, we have already found γ as a function of ϕ , we have on substitution

$$df = \frac{d\gamma}{\pi \sqrt{3 - \gamma^2}} \quad (3)$$

as the distribution of γ for the case $n = 3$, since γ takes any particular value six times as ϕ changes from 0 to 2π .

The distribution is, of course, symmetrical, and has the following even moments

$$\begin{aligned} \mu_2 &= 3/2 \\ \mu_4 &= 27/8 \\ \mu_6 &= 135/16 \\ &\dots\dots\dots \\ \mu_{2s} &= \frac{(s - \frac{1}{2})!}{s! \sqrt{\pi}} \cdot 3^s. \end{aligned}$$

4. The Moments of γ in General.

The exact distribution for $n > 3$ seems not to be expressible simply in terms of known functions. For the moments about the mean (zero) of the distribution we may proceed as follows: let v_n be the variance of the distribution of γ_n , then squaring both sides of equation (1) and averaging over all possible values we find

$$\begin{aligned} v_n = \frac{n^2 (n-3)^2}{(n-1)(n-2)^3} \sin^6 \theta \cdot v_{n-1} + n \cos^6 \theta - \frac{6n}{n-2} \cos^4 \theta \sin^2 \theta \\ + \frac{9n}{(n-2)^2} \cos^2 \theta \sin^4 \theta; \end{aligned}$$

since equation (2) gives the distribution of θ we may now average over all values of θ , by multiplying by the right-hand side of this equation and integrating with respect to θ from 0 to 2π , we then have

$$\begin{aligned} v_n &= \frac{n^2 (n-3)^2}{(n-1)(n-2)^3} \cdot \frac{(n-2)n(n+2)}{(n-1)(n+1)(n+3)} \cdot v_{n-1} \\ &\quad + \frac{1}{(n-1)(n+1)(n+3)} \left\{ n \cdot 1 \cdot 3 \cdot 5 - \frac{6n}{n-2} \cdot 1 \cdot 3 \right. \\ &\quad \left. + \frac{9n}{(n-2)^2} (n-2)n \cdot 1 \right\} \\ &= \frac{n^3 (n+2)(n-3)^2}{(n-2)^2 (n-1)^2 (n+1)(n+3)} v_{n-1} + \frac{6n}{(n-2)(n-1)(n+3)}. \end{aligned}$$

The variance for any particular value of n may now be found by direct substitution ; alternatively we may note that if

$$w_n = \frac{(n-2)^2 (n+1) (n+3)}{n^2} v_n,$$

then

$$w_{n-1} = \frac{(n-3)^2 n (n+2)}{(n-1)^2} v_{n-1},$$

and the recurrence relation is reduced to

$$w_n - w_{n-1} = \frac{6(n-2) (n+1)}{n(n-1)} = 6 + 12 \left(\frac{1}{n} - \frac{1}{n-1} \right);$$

whence

$$w_n = C + 6n + 12/n,$$

where C is a constant to be determined from

$$w_3 = 4;$$

whence

$$w_n = 6 \left(n - 3 + \frac{2}{n} \right) = \frac{6(n-1)(n-2)}{n} \frac{1}{2},$$

and

$$v_n = \frac{6n(n-1)}{(n-2)(n+1)(n+3)},$$

the general formula for the variance of γ_n .

The same process applied to the mean fourth power will give a recurrence formula involving the variance, for which the value found can now be substituted ; in this way the mean values of all even powers may be evaluated in succession. Writing v' for the fourth moment, we have the equation

$$\begin{aligned} v_n' &= \frac{n^4 (n-3)^4}{(n-1)^2 (n-2)^6} \cdot \frac{(n-2) n (n+2) (n+4) (n+6) (n+8)}{(n-1) (n+1) (n+3) (n+5) (n+7) (n+9)} v_{n-1}' \\ &+ \frac{6n^3 (n-3)^2}{(n-1) (n-2)^3} \cdot \frac{6(n^2 - n + 70) n (n+2)}{(n-2)(n-1)(n+1)(n+3)(n+5)(n+7)(n+9)} v_{n-1} \\ &+ \frac{108n^3 (31n^3 - 144n^2 + 183n + 70)}{(n-2)^3 (n-1) (n+1) (n+3) (n+5) (n+7) (n+9)}, \end{aligned}$$

or, substituting for v_{n-1} ,

$$\begin{aligned} v_n' &= \frac{n^5 (n-3)^4 (n+2) (n+4) (n+6) (n+8)}{(n-2)^5 (n-1)^3 (n+1) (n+3) (n+5) (n+7) (n+9)} v_{n-1}' \\ &+ \frac{108n^3 (2n^4 + 23n^3 + 2n^2 - 237n + 70)}{(n-2)^3 (n-1) (n+1) (n+3) (n+5) (n+7) (n+9)}; \end{aligned}$$

but if

$$w_n' = \frac{(n-2)^4 (n+1) (n+3) (n+5) (n+7) (n+9)}{n^4 (n-1)} v_n',$$

then

$$\begin{aligned} w_n' - w_{n+1}' &= \frac{108 (n-2)}{n^2 (n-1)^2} (2n^4 + 23n^3 + 2n^2 - 237n + 70) \\ &= 108 \left\{ 2n + 23 - \frac{264}{n(n-1)} + 140 \frac{2n-1}{n^2(n-1)^2} \right\}, \end{aligned}$$

so that

$$w_n' = 108 \left(n^2 + 24n + C + \frac{264}{n} - \frac{140}{n^2} \right),$$

where C is to be determined from

$$w_3' = 480$$

so that

$$C = -149,$$

$$w_n' = \frac{108 (n-1)(n-2)}{n^2} (n^2 + 27n - 70),$$

and the fourth moment of γ is given by

$$\mu_4(\gamma) = v_n' = \frac{108n^2 (n-1)^2 (n^2 + 27n - 70)}{(n-2)^3 (n+1) (n+3) (n+5) (n+7) (n+9)}.$$

Similarly the sixth moment is found to be

$$\mu_6(\gamma) = \frac{3240n^3 (n-1)^3 (n^4 + 84n^3 + 2695n^2 - 15168n + 20020)}{(n-2)^5 (n+1) (n+3) \dots (n+15)},$$

and the same method may be applied to determine the higher moments.

From the moments the cumulative moment functions may be determined by the invariable relationships, which for symmetrical distributions become

$$\kappa_2 = \mu_2$$

$$\kappa_4 = \mu_4 - 3\mu_2^2$$

$$\kappa_6 = \mu_6 - 15\mu_2\mu_4 + 30\mu_2^3,$$

which give us the values

$$\kappa_2 = \frac{6n(n-1)}{(n-2)(n+1)(n+3)},$$

$$\kappa_4 = \frac{1296n^2(n-1)^2(n-7)(n^2+2n-5)}{(n-2)^3(n+1)^2(n+3)^2(n+5)(n+7)(n+9)},$$

$$\kappa_6 = \frac{466560n^3(n-1)^3(7n^6-88n^5-286n^4+3284n^3+1667n^2-22108n+20020)}{(n-2)^5(n+1)^3(n+3)^3(n+5)(n+7)(n+9)(n+11)(n+13)(n+15)},$$

from which we may derive the ratios,

$$\frac{1}{4!} \kappa_4 \kappa_2^{-2} = \frac{3(n-7)(n^2+2n-5)}{2(n-2)(n+5)(n+7)(n+9)},$$

$$\frac{1}{6!} \kappa_6 \kappa_2^{-3} = \frac{3(7n^6 - 88n^5 - 286n^4 + 3284n^3 + 1667n^2 - 22108n + 20020)}{(n-2)^2(n+5)(n+7)(n+9)(n+11)(n+13)(n+15)},$$

which determine the rate of approach of the distribution of γ to normality as the sample number n is increased. It will be noticed that κ_4 changes from a negative to a positive sign at $n = 7$, and that the corresponding ratio rises to its greatest value about 0.024 at $n = 22$, while the corresponding ratio for κ_6 starting from positive values has a negative maximum about -0.0016 at $n = 8$, is positive again at $n = 13$, and reaches a positive maximum about $+0.0027$ at $n = 32$. Using the reciprocal of n as abscissa the course of these two ratios is shown in figs. 1 and 2.

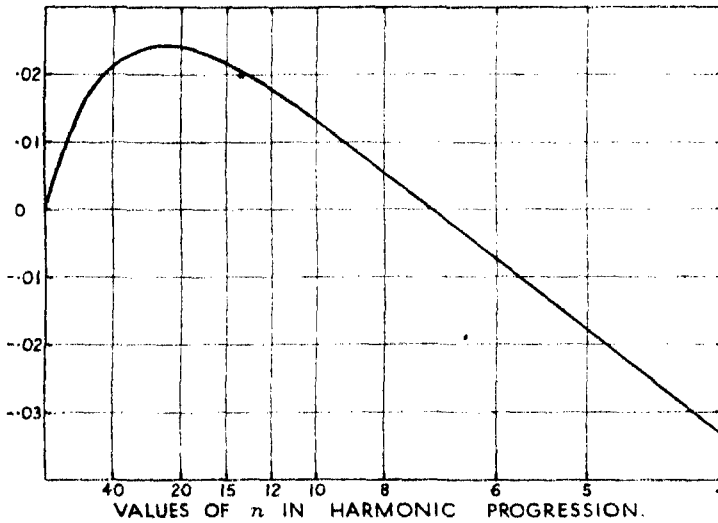


FIG. 1.—Graph of the Ratio $\kappa_4 \kappa_2^{-2} / 4!$ of the distribution of $\gamma = k_2 k_2^{-3} / n$.

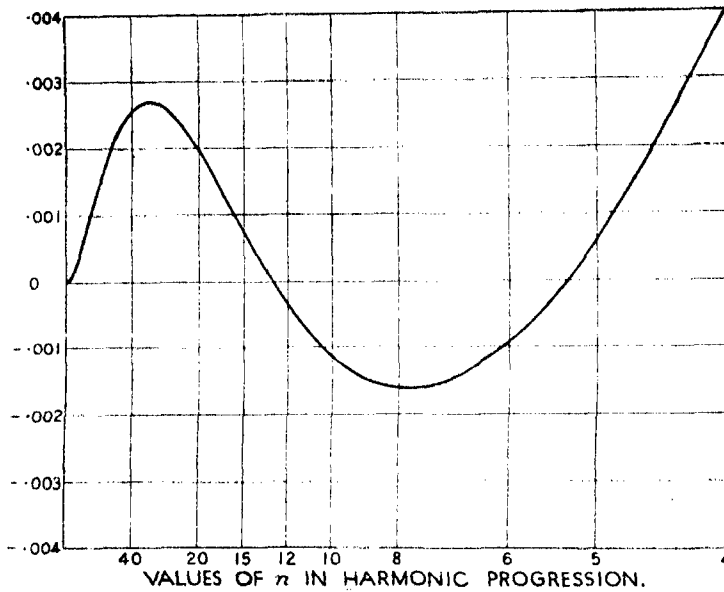


FIG. 2.—Graph of the Ratio $\kappa_3\kappa_2^{-3}/6!$ of the distribution of $\gamma = k_3k_2^{-3/2}$.

5. *The Moments of the Simultaneous Distribution of Different Measures of Departure from Normality.*

It is obvious that the method of approach adopted in the foregoing sections is applicable to the determination of the moments of the distributions of, or more generally of the simultaneous distribution of, all measures of departure from normality such as

$$\gamma = k_3k_2^{-3/2}$$

$$\delta = k_4k_2^{-2}$$

$$\varepsilon = k_5k_2^{-5/2}$$

and so on.

For δ and ε we find the recurrence relations comparable with that already found for γ , namely

$$\gamma_n = n^{1/2} c^3 - \frac{3n^{1/2}}{n-2} c s^2 + \frac{n(n-3)}{(n-2)^{3/2}(n-1)^{1/2}} s^3 \cdot \gamma_{n-1},$$

$$\begin{aligned} \delta_n = n c^4 - \frac{6n}{n-2} c^2 s^2 + \frac{3}{n-2} s^4 - \frac{4n^{1/2}(n+1)}{(n-2)^{3/2}(n-1)^{1/2}} c s^3 \gamma_{n-1} \\ + \frac{(n+1)(n-4)}{(n-2)^2} s^4 \cdot \delta_{n-1}, \end{aligned}$$

$$\begin{aligned}\varepsilon_n = n^{3/2} c^5 \frac{10n^{3/2}}{n-2} c^3 s^2 + \frac{15n^{1/2}}{n-2} c s^4 \frac{10n(n+1)}{(n-2)^{3/2}(n-1)^{1/2}} \left(c^2 s^3 - \frac{s^5}{n+4} \right) \gamma_{n-1} \\ - \frac{5n^{1/2}(n+5)}{(n-2)^2} c s^4 \delta_{n-1} + \frac{n^2(n^2-25)s^5}{(n-2)^{5/2}(n-1)^{1/2}(n+4)} \varepsilon_{n-1},\end{aligned}$$

and by a mere repetition of the algebraic processes employed above, we may obtain a recurrence relation for the mean value of any expression of the form

$$\gamma^a \delta^b \varepsilon^c, \dots,$$

from which the mean value in question may be derived.

If, in accordance with the notation employed for the designation of the moments of the set of statistics $k_2, k_3, k_4, \dots$, we represent such a mean product by

$$\mu (\dots 5^c 4^b 3^a 2^{-r}),$$

where

$$2r = 3a + 4b + 5c + \dots,$$

so that r is always an integer save for the odd moments which necessarily vanish, we may list the following formulæ :

$$\mu (3^2 2^{-3}) = \frac{6n(n-1)}{(n-2)(n+1)(n+3)},$$

$$\mu (4^2 2^{-4}) = \frac{24n(n-1)^2}{(n-3)(n-2)(n+3)(n+5)},$$

$$\mu (4 \ 3^2 2^{-5}) = \frac{216n^2(n-1)^2}{(n-2)^2(n+1)(n+3)(n+5)(n+7)},$$

$$\mu (5^2 2^{-5}) = \frac{120n^2(n+5)(n-1)^3}{(n-4)(n-3)(n-2)(n+1)(n+3)(n+5)(n+7)},$$

$$\mu (3^4 2^{-6}) = \frac{108n^2(n-1)^2(n^2+27n-70)}{(n-2)^3(n+1)(n+3)(n+5)(n+7)(n+9)},$$

$$\mu (4^3 2^{-6}) = \frac{1728n(n-1)^3(n^2-5n+2)}{(n-3)^2(n-2)^2(n+3)(n+5)(n+7)(n+9)},$$

$$\mu (3^6 2^{-9}) = \frac{3240n^3(n-1)^3(n^4+84n^3+2695n^2-15168n+20020)}{(n-2)^5(n+1)(n+3)(n+5)(n+7)(n+9)(n+11)(n+13)(n+15)}.$$

A comparison of these formulæ with those already given (Fisher, 1929), for

the cumulative moment functions of k_2, k_3, k_4 , which in every case but $\mu(3^4)$ and $\mu(3^6)$ are also the moments of the distribution, shows that

$$\begin{aligned}\mu(3^2) &= \frac{6n}{(n-1)(n-2)} \kappa_2^3, \\ \mu(4^2) &= \frac{24n(n+1)}{(n-1)(n-2)(n-3)} \kappa_2^4, \\ \mu(4^3) &= \frac{216n^2}{(n-1)^2(n-2)^2} \kappa_2^5, \\ \mu(5^3) &= \frac{120n^2(n+5)}{(n-1)(n-2)(n-3)(n-4)} \kappa_2^6, \\ \mu(4^4) &= \frac{1728n(n+1)(n^2-5n+2)}{(n-1)^2(n-2)^2(n-3)^2} \kappa_2^6.\end{aligned}$$

Moreover

$$\begin{aligned}\mu(3^4) &= \kappa(3^4) + 3\kappa^2(3^2) \\ &= \left\{ \frac{648n^2(5n-12)}{(n-1)^3(n-2)^3} + \frac{108n^2}{(n-1)^2(n-2)^2} \right\} \kappa_2^6 \\ &= \frac{108n^2(n^2+27n-70)}{(n-1)^3(n-2)^3} \kappa_2^6,\end{aligned}$$

and

$$\begin{aligned}\mu(3^6) &= \kappa(3^6) + 15\kappa(3^4)\kappa(3^2) + 15\kappa^3(3^2) \\ &= 3240\kappa_2^9 \left\{ \frac{144(22n^2-111n+142)n^3}{(n-1)^5(n-2)^5} + \frac{18(5n-12)n^3}{(n-1)^4(n-2)^4} \right. \\ &\quad \left. + \frac{n^3}{(n-1)^3(n-2)^3} \right\} \\ &= \frac{3240n^3(n^4+84n^3+2695n^2-15168n+20020)}{(n-1)^5(n-2)^5} \kappa_2^9.\end{aligned}$$

In every case, therefore, the moment of the distribution of $\gamma, \delta, \epsilon, \dots$, is derivable by multiplying by

$$\frac{(n-1)^r}{(n-1)(n+1)\dots(n+2r-3)} \kappa_2^r$$

the corresponding moment of the distribution of $k_2, k_4, k_6, \dots$. Since many of the latter moments may be found relatively expeditiously by means of the combinatorial procedure, this will be the quicker method for the more complex product moments. For moments of high degree, however, such as (3^8) and (3^{10}) it does not seem easy to enumerate with certainty all the combinatorial

patterns, and the recurrence method, though necessarily heavy, supplies a valuable check.

An analytical proof of this relationship, or at least analytical grounds for accepting it as general, may be found by the method of transforming the characteristic function previously employed in demonstrating the rules of the combinatorial method. If

$$M(t_1, t_2, \dots)$$

is the characteristic function of the simultaneous distribution of the variates $x_1, x_2, \dots$, and if

$$M'(\tau_1, \tau_2, \dots)$$

is that of variates $\xi_1, \xi_2, \dots$, defined in terms of $x_1, x_2, \dots$, by the relations

$$\xi_1 = f_1(x_1, x_2, \dots),$$

$$\xi_2 = f_2(x_1, x_2, \dots),$$

then

$$M'(\tau_1, \tau_2, \dots) = e^{i\tau_1 f_1 + i\tau_2 f_2 + \dots} M(t_1, t_2, \dots)$$

at $t_1 = 0, t_2 = 0, \dots$, where f_p in the index stands for

$$f_p \left(\frac{d}{dt_1}, \frac{d}{dt_2}, \dots \right).$$

To apply this theorem to the present case we utilise the fact that in sampling from the normal distribution k_2 is distributed independently of $\gamma, \delta, \epsilon, \dots$, in the known distribution

$$df = \frac{1}{\frac{1}{2}(n-3)} \cdot \left(\frac{n-1}{2\kappa_2} \right)^{\frac{1}{2}(n-1)} k_2^{\frac{1}{2}(n-3)} e^{-\frac{1}{2}(n-1)k_2/\kappa_2} dk_2,$$

of which the characteristic function,

$$\int e^{it_2} df,$$

is

$$\left(1 - \frac{2\kappa_2 t_2}{n-1} \right)^{-\frac{1}{2}(n-1)}.$$

Hence the general characteristic function of the simultaneous distribution of $k_2, \gamma, \delta, \dots$, is of the form

$$\left(1 - \frac{2\kappa_2 t_2}{n-1} \right)^{-\frac{1}{2}(n-1)} M(t_2, t_3, \dots),$$

where M is the sum of terms such as

$$\mu \dots 5^c 4^b 3^a 2^{-r} \frac{t_2^a t_3^b t_4^c}{a! b! c!} \dots,$$

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and from this expression we must be able to derive the function

$$M'(\tau_3, \tau_4, \dots) = \sum \mu(\dots 5^c 4^b 3^a) \frac{\tau_3^a}{a!} \frac{\tau_4^b}{b!} \frac{\tau_5^c}{c!}$$

by the action of the operator

$$e^{\tau_3 D_3 D_2^{3/2} + \tau_4 D_4 D_2^2 + \tau_5 D_5 D_2^{5/2} + \dots}$$

where D_p stands for d/dt_p .

It appears, therefore, without discussing what meaning should be attached to the fractional indices, which find in fact only zero terms on which to operate, that

$$\mu(\dots 5^c 4^b 3^a) = \mu(\dots 5^c 4^b 3^a 2^{-r}) \cdot \frac{d^r}{dt_2^r} \left(1 - \frac{2\kappa_2 t_2}{n-1}\right)^{-1(n-1)}$$

at $t_2 = 0$, or that

$$\mu(\dots 5^c 4^b 3^a) = \mu(\dots 5^c 4^b 3^a 2^{-r}) \cdot \frac{(n-1) \dots (n+2r-3)}{(n-1)^r} \kappa_2^r,$$

which is the relationship required.

Summary.

Two methods are given for discussing the distribution of the ratios of the symmetric functions $k_3, k_4, \dots$, obtained from samples from a normal distribution to the powers of k_2 of the same degree.

The first method consists in the development of recurrence relations expressing the ratios from a sample of n in terms of the corresponding ratios from a sample of $n-1$ observations, and of a parameter distributed independently in a known distribution. Theoretically all properties of the general distribution could be obtained from these relations in conjunction with a study of samples of 3, 4, 5 ... observations.

The relations are used to derive the exact values of the first three even moments of the simplest ratio γ , and of the simpler non-vanishing moments of the simultaneous distribution of all the ratios. It is observed that these moments are very simply related to the corresponding moments of the distribution of $k_3, k_4, \dots$, given in a previous paper.

The second method is an application of the method of symbolical operators developed by the author, which confirms the generality of the relationship found. The moments of the one distribution may thus be inferred directly from that of the other for which the combinatorial procedure is available.

*The Use of Series of Bessel Functions in Problems connected with
Cylindrical Wind-Tunnels.*

By G. N. WATSON, F.R.S.

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1. There are various series of the types associated with the names of Fourier-Bessel and Dini which arise in the discussion of the problem of a body (the Rankine "Ovoid") placed in a cylindrical wind-tunnel. Four such series are

$$(1) \quad S_1 = \sum_{m=1}^{\infty} \frac{J_0(k_m r)}{J_1^2(k_m a)} e^{-k_m x},$$

$$(2) \quad S_2 = \sum_{m=1}^{\infty} \frac{J_1(k_m r)}{k_m a J_1^2(k_m a)} e^{-k_m x},$$

$$(3) \quad S_3 = \sum_{m=1}^{\infty} \frac{J_0(\kappa_m r)}{J_0^2(\kappa_m a)} e^{-\kappa_m x},$$

$$(4) \quad S_4 = \sum_{m=1}^{\infty} \frac{J_0'(\kappa_m r)}{\kappa_m a J_0^2(\kappa_m a)} e^{-\kappa_m x},$$

where J_0 and J_1 denote Bessel functions of orders 0 and 1; $k_1, k_2, k_3, \dots$, are the positive roots of the equation $J_0(ka) = 0$; $\kappa_1, \kappa_2, \kappa_3, \dots$, are the positive roots of the equation $J_1(\kappa a) = 0$; and, so far as we are concerned, r, a and x are positive with $0 < r < a$. It may be mentioned that a is the radius of the tunnel while r and x are respectively radial and axial coordinates.

It is not my object to discuss the origin of these series, which will be found elsewhere.* It is obvious that the series are rapidly convergent and are well adapted for computation when x is large; but convergence is slow when x is small and (in the case of the first and third) is non-existent when $x = 0$. Mr. C. N. H. Lock, of the National Physical Laboratory, has asked me whether it is possible to express the series in forms which are suitable for computation when x is small—a problem which is evidently of some physical importance—and the investigation presents various features of mathematical interest. Accordingly in this paper I shall show how to express the series as combinations of elementary functions and convergent series of ascending powers of x

* Lamb, "Aeronautical Research Committee Reports and Memoranda," No. 1010 (1926); Lock, *ibid.*, No. 1275 (1930).

and r with coefficients in forms which are fairly well adapted for computation.

2. If $j_1, j_2, j_3, \dots$, denote the positive zeros of $J_0(w)$, we have

$$S_1 = \sum_{m=1}^{\infty} \frac{J_0(j_m r/a)}{J_1^2(j_m)} e^{-j_m x/a}.$$

Now the function*

$$\frac{1}{2} \pi w \{J_0(w) Y_0(rw/a) - J_0(rw/a) Y_0(w)\} / J_0(w)$$

has simple poles at each of the points $w = \pm j_m$, and it is one-valued and analytic at all other points of the w -plane; and its residue at j_m can be proved to be $J_0(j_m r/a) / J_1^2(j_m)$.

Hence, by Cauchy's theorem,

$$S_1 = - \frac{1}{2\pi i} \int_{-\infty i}^{\infty i} \frac{J_0(w) Y_0(rw/a) - J_0(rw/a) Y_0(w)}{J_0(w)} \frac{1}{2} \pi w e^{-xw/a} dw,$$

where the path of integration is the imaginary axis; the integral taken along a large semicircle on the right of the imaginary axis tends to zero when the radius of the semicircle tends to infinity through values such that the semicircle avoids the poles of the integrand.

Now, introducing the modified Bessel functions, we have

$$Y_0(\pm it) = \pm i I_0(t) - \frac{2}{\pi} K_0(t);$$

and so, replacing w by $\pm it$ on the two halves of the imaginary axis, we get

$$\begin{aligned} S_1 &= \frac{1}{\pi} \int_0^{\infty} \frac{I_0(t) K_0(rt/a) - I_0(rt/a) K_0(t)}{I_0(t)} t \sin(xt/a) dt \\ &= \frac{a^2 x}{2(r^2 + x^2)^{3/2}} - \frac{1}{\pi} \int_0^{\infty} \frac{K_0(t)}{I_0(t)} t I_0(rt/a) \sin(xt/a) dt, \end{aligned}$$

the value of

$$\int_0^{\infty} t K_0(rt/a) \sin(xt/a) dt$$

being readily obtained by differentiating Basset's formula†

$$\int_0^{\infty} \cos(bt) \cdot K_0(t) dt = \frac{\frac{1}{2}\pi}{\sqrt{1+b^2}},$$

and making a slight change of notation.

* Cf. Watson, "Theory of Bessel Functions" (1922), § 18·21 (3). The notation of that treatise is used throughout this paper.

† "Hydrodynamics," vol. 2, p. 32 (1889); or Watson, *loc. cit.*, § 13·21 (10).

Now consider the remaining integral; to justify expanding

$$I_0(rt/a) \sin(xt/a)$$

in ascending powers of t/a and integrating term-by-term, we observe that the terms of the series so obtained are numerically less than those in the corresponding series for $I_0(rt/a) \sinh(xt/a)$, which are all positive. Now the integral

$$\int_0^\infty \frac{K_0(t)}{I_0(t)} I_0(rt/a) \sinh(xt/a) dt$$

is convergent when $r + x < 2a$, and so the given integral is expressible as an absolutely convergent series when $r + x < 2a$, the series being obtained by expanding $I_0(rt/a) \sin(xt/a)$ in ascending powers of t/a and integrating term-by-term.

The result of this operation is the expansion

$$(5) \quad S_1 = \frac{a^2 x}{2(r^2 + x^2)^{3/2}} - \frac{\lambda_2 x}{a} - \frac{\lambda_4 x}{a^3} \left(\frac{r^2}{4} - \frac{x^2}{6} \right) - \frac{\lambda_6 x}{a^5} \left(\frac{r^4}{64} - \frac{r^2 x^2}{24} + \frac{x^4}{120} \right) \\ - \frac{\lambda_8 x}{a^7} \left(\frac{r^6}{2304} - \frac{r^4 x^2}{384} + \frac{r^2 x^4}{480} - \frac{x^6}{5040} \right) - \dots,$$

where

$$(6) \quad \lambda_{2n} = \frac{1}{\pi} \int_0^\infty t^{2n} \frac{K_0(t)}{I_0(t)} dt = \frac{1}{(2n+1)\pi} \int_0^\infty \frac{t^{2n} dt}{I_0^2(t)},$$

by a partial integration. A method of computing the coefficients λ_{2n} will be obtained in § 3. The integrals in (6), so far as I know, have never yet been investigated.

By a more elaborate investigation it can be proved that the expansion on the right of (5) is convergent and is equal to S_1 over the more extensive range of values of r and x for which

$$(7) \quad r^2 + x^2 < 4a^2.$$

Take next the series

$$S_2 = \sum_{m=1}^{\infty} \frac{J_1(k_m r)}{k_m a J_1^2(k_m a)} e^{-k_m x} = \sum_{m=1}^{\infty} \frac{J_1(j_m r/a)}{j_m J_1^2(j_m)} e^{-j_m x/a}.$$

An investigation resembling that already given shows that

$$S_2 = -\frac{1}{2\pi i} \int_{-\infty i}^{\infty i} \frac{J_0(w) Y_1(rw/a) - J_1(rw/a) Y_0(w)}{J_0(w)} \frac{1}{2} \pi e^{-xw/a} dw$$

where the contour now has to have an indentation so that it passes on the right of the origin, since the integrand has a simple pole there with residue $-a/r$. Making the radius of the indentation tend to zero and combining the integrals along the two halves of the imaginary axis as before, we get

$$\begin{aligned} S_2 &= \frac{a}{2r} - \frac{1}{\pi} \int_0^\infty \frac{I_0(t) K_1(rt/a) + I_1(rt/a) K_0(t)}{I_0(t)} \sin(xt/a) dt \\ &= \frac{a}{2r} - \frac{ax}{2r\sqrt{(r^2+x^2)}} - \frac{1}{\pi} \int_0^\infty \frac{K_0(t)}{I_0(t)} I_1(rt/a) \sin(xt/a) dt, \end{aligned}$$

and hence

$$\begin{aligned} (8) \ S_2 &= \frac{a}{2r} - \frac{ax}{2r(r^2+x^2)} - \frac{\lambda_2 rx}{2a^2} - \frac{\lambda_4 rx}{a^4} \left(\frac{r^2}{16} - \frac{x^2}{12} \right) - \frac{\lambda_6 rx}{a^6} \left(\frac{r^4}{384} - \frac{r^2 x^2}{96} + \frac{x^4}{240} \right) \\ &\quad - \frac{\lambda_8 rx}{a^8} \left(\frac{r^6}{18432} - \frac{r^4 x^2}{2304} + \frac{r^2 x^4}{1920} - \frac{x^6}{10080} \right) - \dots, \end{aligned}$$

the range of convergence being given by (7).

Take next the series S_3 ; if $j_{1,1}, j_{1,2}, j_{1,3}, \dots$, denote the positive zeros of $J_1(w)$, then

$$S_3 = \sum_{m=1}^{\infty} \frac{J_0(j_{1,m}r/a)}{J_1^2(j_{1,m})} e^{-j_{1,m}x/a},$$

and the general term of this series is the residue at $j_{1,m}$ of

$$\frac{J_1(w) Y_0(rw/a) - J_0(rw/a) Y_1(w)}{J_1(w)} \frac{1}{2} \pi w e^{-xw/a}.$$

Hence

$$S_3 = -\frac{1}{2\pi i} \int_{-\infty i}^{\infty i} \frac{J_1(w) Y_0(rw/a) - J_0(rw/a) Y_1(w)}{J_1(w)} \frac{1}{2} \pi w e^{-xw/a} dw,$$

the contour having an indentation at the origin since the integrand has a simple pole there with residue 2.

Modifying the integral as in the investigation of S_2 , we get

$$\begin{aligned} S_3 &= -1 + \frac{1}{\pi} \int_0^\infty \frac{I_1(t) K_0(rt/a) + I_0(rt/a) K_1(t)}{I_1(t)} t \sin(xt/a) dt \\ &= -1 + \frac{a^2 x}{2(r^2+x^2)^{3/2}} + \frac{1}{\pi} \int_0^\infty \frac{K_1(t)}{I_1(t)} I_0(rt/a) \sin(xt/a) dt. \end{aligned}$$

Consequently

$$(9) \quad S_3 = -1 + \frac{a^2 x}{2(r^2 + x^2)^{3/2}} + \frac{\mu_2 x}{a} + \frac{\mu_4 x}{a^3} \left(\frac{r^2}{4} - \frac{x^2}{6} \right) + \frac{\mu_6 x}{a^5} \left(\frac{r^4}{64} - \frac{r^2 x^2}{24} + \frac{x^4}{120} \right) \\ + \frac{\mu_8 x}{a^7} \left(\frac{r^6}{2304} - \frac{r^4 x^2}{384} + \frac{r^2 x^4}{480} - \frac{x^6}{5040} \right) + \dots,$$

where

$$(10) \quad \mu_{2n} = \frac{1}{\pi} \int_0^\infty t^{2n} \frac{K_1(t)}{I_1(t)} dt = \frac{1}{(2n+1)\pi} \int_0^\infty \frac{t^{2n} dt}{I_1^2(t)},$$

and the range of convergence is given by (7). A method of computing the coefficients μ_{2n} will be obtained in § 3.

Lastly, take the series S_4 ; we have

$$S_4 = - \sum_{m=1}^{\infty} \frac{J_1(j_{1,m} r/a)}{j_{1,m} J_2^2(j_{1,m})} e^{-j_{1,m} x/a},$$

and hence

$$S_4 = \frac{1}{2\pi i} \int_{-\infty i}^{\infty i} \frac{J_1(w) Y_1(rw/a) - J_1(rw/a) Y_1(w)}{J_1(w)} \cdot \frac{1}{2} \pi e^{-xw/a} dw,$$

the contour having an indentation at the origin since the integrand has a simple pole there with residue $\frac{r}{a} - \frac{a}{r}$.

Modifying the integral as in the investigation of S_2 , we get

$$S_4 = - \frac{a^2 - r^2}{2ar} + \frac{1}{\pi} \int_0^\infty \frac{I_1(t) K_1(rt/a) - I_1(rt/a) K_1(t)}{I_1(t)} \sin(xt/a) dt \\ = - \frac{a^2 - r^2}{2ar} + \frac{ax}{2r \sqrt{(r^2 + x^2)}} - \frac{1}{\pi} \int_0^\infty \frac{K_1(t)}{I_1(t)} I_1(rt/a) \sin(xt/a) dt$$

Consequently

$$(11) \quad S_4 = - \frac{a^2 - r^2}{2ar} + \frac{ax}{2r \sqrt{(r^2 + x^2)}} - \frac{\mu_2 r x}{2a^2} - \frac{\mu_4 r x}{a^4} \left(\frac{r^2}{16} - \frac{x^2}{12} \right) \\ - \frac{\mu_6 r x}{a^6} \left(\frac{r^4}{384} - \frac{r^2 x^2}{96} + \frac{x^4}{240} \right) \\ - \frac{\mu_8 r x}{a^8} \left(\frac{r^6}{18432} - \frac{r^4 x^2}{2304} + \frac{r^2 x^4}{1920} - \frac{x^6}{10080} \right) - \dots,$$

the range of convergence being given by (7).

Now let

$$f_1(r, x, a) = \frac{S_1}{\frac{a^2}{r^2} - \frac{2a}{r} S_2}, \quad f_2(r, x, a) = \frac{1 + S_2}{\frac{a^2}{r^2} - 1 + \frac{2a}{r} S_4}.$$

It was mentioned to me by Mr. Lock that, if we considered the problem in which the barrier formed by the tunnel was absent, we might anticipate that

$$\lim_{a \rightarrow \infty} f_1(r, x, a) = \frac{r^2}{2(r^2 + x^2)}, \quad \lim_{a \rightarrow \infty} f_2(r, x, a) = \frac{r^2}{2(r^2 + x^2)};$$

and these conjectures are confirmed by the expansions which have been obtained. He also suggested the possibility that

$$\frac{a^3}{r^3} \left\{ \frac{1 + f_1(r, x, a)}{1 + f_1(r, x, \infty)} - 1 \right\}, \quad \frac{a^3}{r^3} \left\{ \frac{1 + f_2(r, x, a)}{1 + f_2(r, x, \infty)} - 1 \right\},$$

might tend to limits when $a \rightarrow \infty$; and, in fact, it is not difficult to deduce from the various expansions that

$$\lim_{a \rightarrow \infty} \frac{a^3}{r^3} \left\{ \frac{1 + f_1(r, x, a)}{1 + f_1(r, x, \infty)} - 1 \right\} = -\lambda_2 \frac{\sqrt{(r^2 + x^2)}}{r},$$

$$\lim_{a \rightarrow \infty} \frac{a^3}{r^3} \left\{ \frac{1 + f_2(r, x, a)}{1 + f_2(r, x, \infty)} - 1 \right\} = \mu_2 \frac{\sqrt{(r^2 + x^2)}}{r},$$

3. We are still faced with the problem of reducing the constants λ_{2n} and μ_{2n} to forms suitable for computation; the Euler-Maclaurin sum-formula is useless, and the similar, but more powerful, summatory formula due to Plana needs considerable modification before it can be used. It therefore seemed advisable to construct a direct method which gives results of a type which would be obtained much more laboriously by modifying Plana's formula. The method is applicable to the more general integral

$$\frac{1}{\pi} \int_0^\infty \frac{t^{2\nu+2r} dt}{I_\nu^2(t)}$$

(where r is any of the integers 0, 1, 2, 3, ..., and* $\nu > -1$), which we now show how to evaluate as a fairly rapidly convergent series.

The initial step consists in expressing†

$$\frac{t^{2\nu+2r}}{I_\nu^2(t) \cos(\pi t/\alpha)}$$

as a sum of partial fractions, where α is a positive constant which will be fixed later to suit our convenience.

It is easy to see that

$$\frac{1}{2\pi i} \int \frac{w^{2\nu+2r} dw}{(w-t) I_\nu^2(w) \cos(\pi w/\alpha)},$$

* It is unnecessary to restrict ν to integral values.

† The actual generalisation of Plana's formula is obtained by replacing the cosine by a sine; the use of the cosine makes the analysis and the resulting formula slightly simpler.

when taken round the circle $|w| = R$, tends to zero when R tends to infinity through a sequence of values such that the circle never passes through any pole of the integrand. The poles are

$$w = t, \quad w = \pm ij_m, \quad w = \pm (n + \frac{1}{2})\alpha,$$

where* $j_1, j_2, j_3, \dots$, are the positive zeros of $J_\nu(w)$; and $m = 1, 2, 3, \dots$, $n = 0, 1, 2, \dots$.

It follows that the sum of the residues of the integrand at all of its poles is zero. The residue at $w = t$ is

$$\frac{t^{2\nu+2r}}{I_\nu^2(t) \cos(\pi t/\alpha)},$$

the residues at $w = \pm (n + \frac{1}{2})\alpha$ are

$$-\frac{(-)^n (n + \frac{1}{2})^{2\nu+2r+1} \alpha^{2\nu+2r+1}}{\pi (n\alpha + \frac{1}{2}\alpha \mp t) I_\nu^2(n\alpha + \frac{1}{2}\alpha)},$$

and the residues at $w = \pm ij_m$ are

$$-\frac{(-)^r j_m^{2\nu+2r-1}}{J_{\nu+1}^2(j_m/\alpha) \cosh(\pi j_m/\alpha)} \left[\frac{j_m}{(j_m \pm it)^2} - \frac{2\nu + 2r + 1 - (\pi j_m/\alpha) \tanh(\pi j_m/\alpha)}{j_m \pm it} \right].$$

Consequently

$$\begin{aligned} \frac{t^{2\nu+2r}}{I_\nu^2(t) \cos(\pi t/\alpha)} &= \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{(-)^n (n + \frac{1}{2})^{2\nu+2r+1} \alpha^{2\nu+2r+2}}{\{(n\alpha + \frac{1}{2}\alpha)^2 - t^2\} I_\nu^2(n\alpha + \frac{1}{2}\alpha)} \\ &\quad + 2(-)^r \sum_{m=1}^{\infty} \frac{j_m^{2\nu+2r}}{J_{\nu+1}^2(j_m/\alpha) \cosh(\pi j_m/\alpha)} \\ &\quad \times \left[\frac{j_m^2 - t^2}{(j_m^2 + t^2)^2} - \frac{2\nu + 2r + 1 - (\pi j_m/\alpha) \tanh(\pi j_m/\alpha)}{j_m^2 + t^2} \right]. \end{aligned}$$

Multiply by $\cos(\pi t/\alpha)$ and integrate; it follows that

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{t^{2\nu+2r} dt}{I_\nu^2(t)} &= \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{(-)^n (n + \frac{1}{2})^{2\nu+2r+1} \alpha^{2\nu+2r+2}}{I_\nu^2(n\alpha + \frac{1}{2}\alpha)} \int_{-\infty}^{\infty} \frac{\cos(\pi t/\alpha) dt}{(n\alpha + \frac{1}{2}\alpha)^2 - t^2} \\ &\quad + 2(-)^r \sum_{m=1}^{\infty} \frac{j_m^{2\nu+2r}}{J_{\nu+1}^2(j_m/\alpha) \cosh(\pi j_m/\alpha)} \left[\int_{-\infty}^{\infty} \frac{(j_m^2 - t^2) \cos(\pi t/\alpha) dt}{(j_m^2 + t^2)^2} \right. \\ &\quad \left. - \{2\nu + 2r + 1 - (\pi j_m/\alpha) \tanh(\pi j_m/\alpha)\} \int_{-\infty}^{\infty} \frac{\cos(\pi t/\alpha) dt}{j_m^2 + t^2} \right]. \end{aligned}$$

* It would be more precise to write $j_{\nu, m}$ in place of j_m ; but the omission of the suffix ν will not lead to confusion and will simplify and improve the appearance of various formulæ.

Now

$$\begin{aligned}
 \int_{-\infty}^{\infty} \frac{\cos (\pi t / \alpha) d t}{(n \alpha+\frac{1}{2} \alpha)^2-t^2} &= \frac{1}{\alpha} \int_{-\infty}^{\infty} \frac{\cos \pi u d u}{(n+\frac{1}{2})^2-u^2} \\
 &= \frac{1}{2 \alpha\left(n+\frac{1}{2}\right)}\left[\int_{-\infty}^{\infty} \frac{\cos \pi u d u}{u+\left(n+\frac{1}{2}\right)}-\int_{-\infty}^{\infty} \frac{\cos \pi u d u}{u-\left(n+\frac{1}{2}\right)}\right] \\
 &= \frac{(-)^n}{2 \alpha\left(n+\frac{1}{2}\right)}\left[\int_{-\infty}^{\infty} \frac{\sin \pi t d t}{t}+\int_{-\infty}^{\infty} \frac{\sin \pi t d t}{t}\right] \\
 &= \frac{(-)^n \pi}{\alpha\left(n+\frac{1}{2}\right)},
 \end{aligned}$$

and

$$\begin{aligned}
 \int_{-\infty}^{\infty} \frac{\cos (\pi t / \alpha) d t}{j_m^2+t^2} &= \frac{\pi}{j_m} \exp (-\pi j_m / \alpha), \\
 \int_{-\infty}^{\infty} \frac{\left(j_m^2-t^2\right) \cos (\pi t / \alpha) d t}{\left(j_m^2+t^2\right)^2} &= \frac{\pi^2}{\alpha} \exp (-\pi j_m / \alpha).
 \end{aligned}$$

It is consequently evident that

$$\begin{aligned}
 \int_{-\infty}^{\infty} \frac{t^{2 \nu+2 r} d t}{I_{\nu}^2(t)} &= 2 \alpha \sum_{n=0}^{\infty} \frac{\left(n \alpha+\frac{1}{2} \alpha\right)^{2 \nu+2 r}}{I_{\nu}^2\left(n \alpha+\frac{1}{2} \alpha\right)} \\
 &+ 2 \pi(-)^r \sum_{m=1}^{\infty} \frac{j_m^{2 \nu+2 r-1} \exp (-\pi j_m / \alpha)}{J_{\nu+1}^2\left(j_m\right) \cosh \left(\pi j_m / \alpha\right)} \\
 &\times\left[\pi j_m / \alpha-(2 \nu+2 r+1)+\left(\pi j_m / \alpha\right) \tanh \left(\pi j_m / \alpha\right)\right],
 \end{aligned}$$

and therefore

$$\begin{aligned}
 \frac{1}{\pi} \int_0^{\infty} \frac{t^{2 \nu+2 r} d t}{I_{\nu}^2(t)} &= \frac{\alpha}{\pi} \sum_{n=0}^{\infty} \frac{\left(n \alpha+\frac{1}{2} \alpha\right)^{2 \nu+2 r}}{I_{\nu}^2\left(n \alpha+\frac{1}{2} \alpha\right)} \\
 &+(-)^r \sum_{m=1}^{\infty} \frac{j_m^{2 \nu+2 r-1}}{J_{\nu+1}^2\left(j_m\right)}\left[\frac{\pi j_m / \alpha}{\cosh ^2\left(\pi j_m / \alpha\right)}\right. \\
 &\quad \left.-\left(2 \nu+2 r+1\right) \frac{\exp \left(-\pi j_m / \alpha\right)}{\cosh \left(\pi j_m / \alpha\right)}\right],
 \end{aligned}$$

which is the desired result.

The first of the series on the right converges rapidly when α is large, the second when α is small; but it is more tedious to compute the terms of the second series than those of the first. A reasonable compromise appears to be to take $\alpha = 1$.

The following results were obtained by taking $\alpha = 1$, and were checked by taking $\alpha = 1.2$:

$$\begin{aligned}\frac{1}{\pi} \int_0^\infty \frac{t^2 dt}{I_0^2(t)} &= 0.6177337, & \frac{1}{\pi} \int_0^\infty \frac{t^4 dt}{I_0^2(t)} &= 3.2942841, \\ \frac{1}{\pi} \int_0^\infty \frac{t^2 dt}{I_1^2(t)} &= 2.3904725, & \frac{1}{\pi} \int_0^\infty \frac{t^4 dt}{I_1^2(t)} &= 6.0023517.\end{aligned}$$

From these results it follows that

$$\begin{aligned}\lambda_2 &= 0.2059112, & \lambda_4 &= 0.6588568, \\ \mu_2 &= 0.7968242, & \mu_4 &= 1.2004703.\end{aligned}$$

I must express my thanks to Mr. Lock for bringing to my notice the problems discussed in this paper.

Thunder-storms and the Penetrating Radiation.

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[PLATE I.]

§ 1. *Introduction.*

The possibility of a connection between thunder-storms and the penetrating radiation was first suggested by C. T. R. Wilson,* who pointed out that the powerful fields within thunder-storms should exert an important accelerating effect upon β -particles produced by the disintegration of the radioactive material carried in the air. He showed that many of these particles should gain far more energy from the field in traversing a given distance than they lost in ionisation, and that they might thus acquire a very considerable fraction of the energy corresponding to the fall of potential, of the order of 10^9 volts, between the poles of the cloud. He examined the effect of close encounters of these accelerated particles with atomic electrons, resulting in the ejection of fast secondary particles, and also the action of ordinary nuclear scattering, and found that neither of these would seriously interfere with the accelerating process. The secondary electrons, indeed, would often be emitted with

* 'Proc. Camb. Phil. Soc.,' vol. 22, p. 534 (1925).

sufficient energy and in a suitable direction to be accelerated themselves. An occasional encounter with an atomic nucleus at a distance at which the inverse square law of force failed to hold would be the only possible manner in which the process might be stopped, but such an encounter would be so rare that the β -particle would have acquired a very considerable amount of energy before it occurred and this might be radiated as a penetrating γ -ray quantum. "The general effect of an accelerating field is that a β -particle, instead of dying as it were a natural death by gradual loss of energy, is continually acquiring more and more energy and increasing its chance of surviving all accidents other than direct encounters with the nuclei of atoms."* In this paper these accelerated particles will be referred to as runaway electrons, a description first applied to them by Eddington.†

Interest in this suggestion, which, as Wilson pointed out, might bear on the question of the origin of part at least of the penetrating radiation, is heightened by the fact that recent estimates of the energy of this radiation considered either as γ - or β -rays give results of the order of 10^9 e.-volts.

Since the fields which prevail within the majority of thunder-clouds are directed downwards, an upward-moving beam of runaway electrons is to be anticipated, passing into the upper air through the top of the cloud. A direct test of the existence of this beam would be very difficult, but it seemed probable that the effect could also occur in the upwardly directed or negative field between the base of the cloud and the ground. In this case a downward-moving beam could be expected and might be detected by its ionising action at the earth's surface. Measurements of the fields below South African thunderstorms‡ have shown that they are practically always negative in sign and though reduced in strength at the ground by the presence of positive ions arising from point-discharge, they should attain the magnitude necessary for the production of the effect over a considerable region below the base of the cloud.

Given a sufficiently sensitive method of measuring the ionisation within a closed vessel, one might therefore hope to detect the presence of downward-moving runaway electron beams by an increase in the ionisation whenever the field below the cloud approached the critical sparking value. Such electrons would have an energy of the same order as those projected upwards, 10^9 e.-volts, and a probable range in air at N.T.P. of 7.7 km. They should,

* 'Proc. Camb. Phil. Soc.,' vol. 22, p. 534 (1925).

† 'Nature,' Supplement, May 1, 1926.

‡ Schonland, 'Proc. Roy. Soc.,' A, vol. 118, p. 233 (1928).

therefore, easily penetrate the walls of an ionisation vessel and produce some 40 ions per centimetre of path in ordinary air.

Experiments of this nature are described in this paper, which have yielded a negative result in so far as downward-moving runaway electrons are concerned. At the same time an effect of opposite character has been found, for it appears that a thunder-storm is sometimes able to stop a very large fraction of the ordinary penetrating radiation which passes through it.

As the electrical conditions in a thunder-storm alter rapidly, the investigation of these two questions requires an extremely sensitive method of measuring the ionisation. Even the observation of integrated effects must be limited to a space of time which is unusually short in penetrating ray measurements, for the cloud is seldom stationary overhead. Such short period observations introduce difficulties because the ordinary fine-weather ionisation itself shows fluctuations due to various causes, and the technique of the measurements thus raises problems which do not usually occur in observations of the intensity of the penetrating rays.

§ 2. *Apparatus.*

The apparatus used to measure the ionisation was based upon the well-known principle of an ionisation-chamber with an electroscope leaf attached to its central electrode. This electroscope, which has been described elsewhere,* consisted of a very light mirror of silvered mica hung by two fine gold-leaf hinges from a bridge on the electrode. Its movement was observed by means of a lamp and scale instead of the usual microscope, and this fact gave two important advantages to the arrangement. In the first place there was no restriction placed upon the volume of the ionisation vessel, which could be made as large as was desired and could contain a wire cage of the type introduced by Hoffmann.† In the second the mirror, and so the capacity of the central electrode, could be made very small without loss of voltage sensitivity since only the angular movement of the leaf was involved. In this way the electroscope could be made sufficiently sensitive to show the effects of individual α -particles upon the ionisation, the spot of light showing sudden measurable jumps when α -particles occurred.

These features of the measuring system made it possible to overcome one cause of the fluctuations referred to in the previous section, namely, the probability variations in the number and the ionisation due to α -particles,

* Schonland, 'Proc. Camb. Phil. Soc.', vol. 25, p. 340 (1929).

† 'Ann. Physik,' vol. 80, p. 779 (1926).

by eliminating these main sources of the residual ionisation altogether. The use of a wire cage at a distance from the walls of the vessel proper, combined with a filling of carbon dioxide from a gas-cylinder, cut down the number of α -particles to about one in every 2 or 3 minutes, and the effects of those that remained could be directly determined and subtracted from the total ionisation.

The ionisation chamber, shown in fig. 1, had an outer casing of cast iron 6 mm. thick, in the form of a cylinder of internal diameter and height both

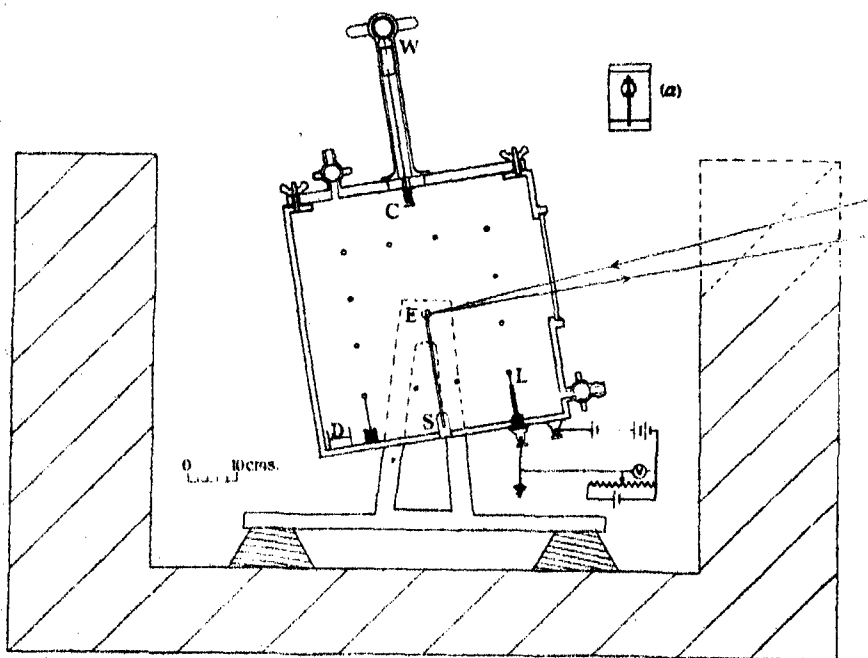


Fig. 1.

25 cm. The top, which was 10 mm. thick, was secured when in use by eight nuts pressing it upon a rubber gasket, and could be removed to enable cage and central electrode to be lifted out. The cage was another cylinder, of diameter and height both 15 cm., and had a volume of 2.65 litres. It was made of zinc-coated wire 0.15 cm. in diameter with gaps measuring 5 cm. by 6 cm., and it was soldered together with pure zinc. It was held in position by four legs, three of which were pushed into ebonite sockets, while the fourth, L, entered a brass holder which made electrical connection with a terminal outside, through an ebonite bushing. It was best cleaned of radioactive deposit by scraping with a razor blade.

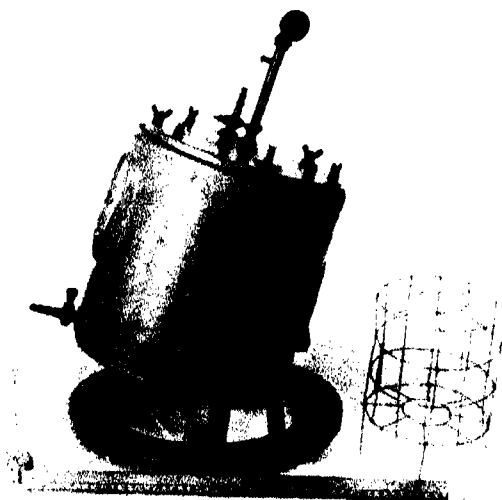


FIG. 2.

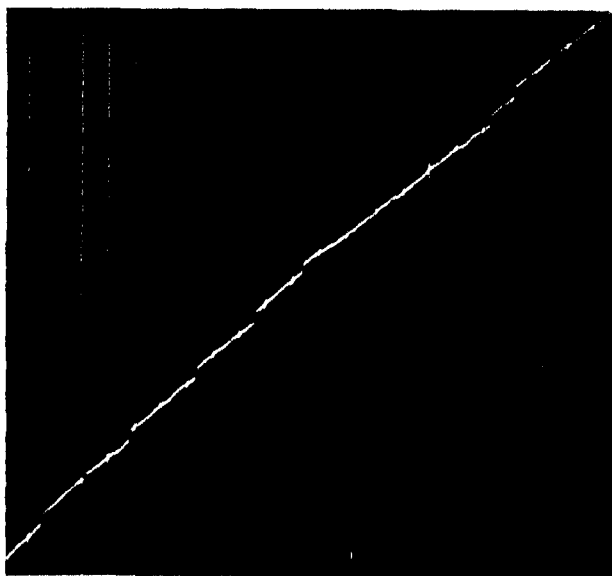


FIG. 3.

At the centre of the vessel was the electrode E, carrying the hinged mirror and supported on a quartz rod of diameter 2.0 mm. This rod was held in a small straight-jawed chuck S. The electrode was made of chemically pure zinc and in shape was a rough sphere of diameter 7 mm., the face next the mirror being flattened. A small hole in the base of E fitted on to the conically ground top of the quartz rod so that the electrode could be quickly removed for alteration or replacement. Charging was done by means of the "vacuum" windlass W, made entirely of brass, which raised or lowered a steel rod at the end of which was a springy platinum contact C. A light spiral of copper wire ensured good connection by joining this contact to the outer case.

The electroscope leaf was a rectangular strip of mica thin enough to show Newton's colours and measuring 3 mm. by 2 mm. It was silvered on both sides and the movement, which took place in a vertical plane, was observed with the aid of a lamp and a semi-transparent scale. Since these mirrors possess cylindrical curvature, the lamp was fitted with a converging lens in front of which a fine slit could be rotated until its length was perpendicular to the axis of the cylinder. A very sharp line could be obtained under these conditions, and by observing a fine diffraction band within it through a suitably mounted short-focus lens, measurements could usually be made with an accuracy of the order of one-tenth of a millimetre.

The whole instrument could be tilted about a horizontal axis by means of a tangent screw in order to increase the sensitivity of the leaf. The voltage sensitivity employed varied between 15 and 25 mm. per volt with the scale at a distance of 1.5 metres. The supporting framework of the instrument rested upon three large rubber corks to cut out the effects of vibration, and the outside was covered with a thick layer of cotton-wool to avoid disturbances of the leaf by air-currents caused by sudden changes of temperature. Fig. 2, Plate 1, shows the completed instrument, with cage and electrode removed.

The vessel was filled with CO_2 from a high pressure cylinder; fresh gas was streamed through it for 10 minutes and it was then shut off at a pressure a few millimetres above that of the atmosphere, usually 62.3 cm. This streaming through was carried out every morning, for it was found that the radio-active content of the gas in the chamber, as indicated by the number of α -particle jumps, grew slowly with time. This was presumably due to an evolution of emanations from the walls of the vessel and has previously been noticed by Hoffmann.* The gas was dried by means of P_2O_5 in the shallow dish D and its pressure was read on a mercury manometer.

* 'Ann. Physik,' vol. 62, p. 756 (1920).

The outer case and the central electrode were positively charged to a potential of about 400 volts, the former being permanently connected to the battery. The cage and the negative end of the battery were earthed, thus there could be no photoelectric emission from the zinc electrode E under the action of the beam of light. The distance between the cage and the walls of the vessel was 5.0 cm., so practically all the α -particles from the walls were stopped before they could enter the space within the cage.

The measurements were made during the summer of 1929-30 at Johannesburg, 1780 metres above sea-level and 8.5 equivalent metres of water below the top of the atmosphere. Two complete central electrodes E, with mica mirrors attached, were carried without damage on the train journey of 1,000 miles from Capetown. They were mounted in glass tubes as shown in fig. 1 (a).

Through the kindness of Prof. Paine, the apparatus was installed in an upper room in the Physics Department of the University of the Witwatersrand. The walls to north and east were of brick (40 cm.) and concrete (20 cm.) while those to south and west were of brick alone (15 cm.). The roof was made of iron sheet 0.3 mm. thick and the ceiling of asbestos 2.0 mm. thick. Screening from local γ -radiation was effected by placing the instrument on a large iron slab 9 cm. thick and surrounding it with a rampart of iron blocks 15 cm. thick, as shown in the figure. This left the chamber open to a vertical cone of half-angular aperture 66° measured from the central electrode. The question of local radiation is further discussed in § 8.

§ 3. *Observations of Electric Fields.*

A simple arrangement was installed in order to be able to correlate changes in the ionisation current with changes in the electrification and distance of the storm. A small pointed lightning conductor fixed in insulators on the roof of the building was joined by cable to one terminal of a d'Arsonval galvanometer, the other terminal of which was earthed. One could infer the sign and general order of magnitude of the electric field below the cloud from the deflection due to point discharge currents, though no absolute determination was possible. In addition, sudden ballistic kicks showed the effects of the sudden changes of field caused by lightning discharges and these were used to obtain the lightning-thunder interval and hence the distance of the storm.

Further information on the electrification of the clouds was obtained from a continuously recording electrometer with a radioactive collector and from photographic records of the field changes made with a capillary electrometer

by the method of C. T. R. Wilson.* These two instruments were being used by Mr. E. L. Halliday in an investigation of the polarity of the thunder-clouds.

§ 4. Method of Observation.

The time of a complete observation was fixed at 10 minutes and during this period a continuous watch was kept upon the spot of light, its position being recorded every minute and a note being made of each sudden jump due to the occurrence of an α -particle. Calling D the total movement during the 10 minutes and $\Sigma\alpha$ the sum of the effects of the α -particles, the quantity $D - \Sigma\alpha$ should represent the ionisation due to the penetrating radiation, plus a small residual ionisation arising from local γ -radiation which will be discussed later.

The observations were made by eye and were very tiring. The apparatus has since been adapted for photographic recording and fig. 3, Plate 1, shows the nature of the movement and some α -particle jumps. This record was taken at sea-level with the instrument unshielded.

While one observer watched the scale, a second observer called the minutes and wrote down the readings and the α -particle jumps called out by the first. This second observer also made a record of the deflections and kicks of the galvanometer and of the distance of the storm. An example of the record of such a 10-minute observation is shown below.

Table I.—Record of a 10-minute Reading.

Minutes.	Scale reading.	α -particle jumps.	1-minute movements.	Galvanometer reading.	Sign of field changes.	Lightning-thunder interval.
	mm.	mm.	mm.	cm.		seconds
0	132.0					
1	127.7	1.2	3.1	—7	—, —	18
2	123.7	1.3	3.7	—5	—	
3	188.5		4.2	—7	+	
4	114.8		3.7	—11	+	
5	111.2		3.6	—10, —14		
6	107.3		3.9	—8, —11, —14	—	20
7	103.9		3.4	—11	+	22
8	99.6	0.4	3.9	0, —2, —11	—, +	
9	96.2		3.4	—14	—	
10	92.9		3.3	—10	+	17

$D = 39.1$ mm.

$\Sigma\alpha = 2.9$ mm.

$[D - \Sigma\alpha]/10 = 3.62$ mm. per minute.

Prevailing field : strong negative.

Distance of storm, 5 to 6 km.

Pressure, 62.25 mm.

* Wilson, 'Phil. Trans.,' A, vol. 221, p. 73 (1921).

The fourth column in this table shows the movement which took place during each single minute, corrected for the α -particle effects which occurred. Though these 1-minute readings were not used in finding $D - \Sigma\alpha$, they proved of value in connection with the question of short period fluctuations and in other ways.

The α -particle jumps were easily distinguishable on account of their extreme suddenness and after a little practice one could feel confident of determining each with an accuracy of ± 0.1 mm. The average number of jumps occurring in 10 minutes was four* and the ratio of $\Sigma\alpha$ to the total fall D about $1/13$, as in the example given in the table. Even if an error of 0.2 mm. had been made in the same direction in estimating each jump in this example, the error in $D - \Sigma\alpha$ would have been no more than 0.6 mm. in 36.2 mm. or 1.6 per cent.

As a direct check upon the accuracy of the method, we may compare the rate of fall during periods free from α -particles with the corrected rate during periods in which jumps occurred. Thus in the case shown in the table, the seven undisturbed minutes gave an average rate of 3.64 mm. per minute, while the three disturbed minutes gave an average corrected rate of 3.57 mm. per minute. This agreement is partly accidental, for one would expect fluctuations over such short periods, and a more satisfactory comparison, made with a larger number of readings and avoiding thunder-storm periods, is given below :—

Total time of observation	210 minutes.
Total fall, D , ...	867.6 mm.
Total α -particle effect, $\Sigma\alpha$	74.9 mm.
Corrected total fall, $D - \Sigma\alpha$	792.7 mm.
Undisturbed period	145 minutes.
Fall during undisturbed period	552.5 mm.
Calculated corrected total fall in 210 minutes	$552.5 \times 210/145 = 800.1$ mm.

Error in observation of $\Sigma\alpha$, $800.1 - 792.7$ mm. = 7.4 mm. This error is 10 per cent., and it appears that the average α -particle jump of 1.0 mm. has been underestimated by 0.1 mm. Since the corrected rate of fall during the whole 210 minutes differs from the rate during the undisturbed period by less than 1 per cent. it is clear that the expected accuracy has been attained. It will be shown in § 6 that fluctuations in the intensity of the penetrating rays themselves are responsible for uncertainties a good deal larger than this.

* G. Hoffmann (*loc. cit.*) found 3 per hour in 250 c.c. of CO_2 equivalent to 5 per 10 minutes in the present case.

In the earlier stages of the work the α -particle effect was larger, the ratio of $\Sigma\alpha$ to D being about 1/7, and the values given above refer to observations made after January 21 (storm 10) when the number of α -particles had been reduced by half as a result of cleaning the inside of the cage.

After a 10-minute observation the electrode was recharged, so that all runs were taken over the same portion of the scale and involved a fall of potential of about 1.5 volts. The insulation provided by the quartz rod was tested by comparing measurements made when the case and the lower end of this rod were at the original charging potential V, with others when they were at $V - 20$ and $V - 40$ volts, but no appreciable difference was observed. A soaking-up effect was noticed on first charging the electrode and this was avoided by keeping it permanently charged, day and night, except during an actual observation.

§ 5. Sensitivity and Reduction Factor for Ionisation.

Instruments of small capacity present well-known difficulties in the accurate determination of the factor to convert scale readings into quantities of electricity and thence to ions per cubic centimetres. In the present case not only the capacity but also the voltage sensitivity was difficult to determine accurately. The charging rod was designed in the first instance to prevent any possibility of damage to the mirror, and the distribution of the charge on the electrode with and without the charging rod in contact were not the same. Since, however, an accurate absolute value of the intensity of the penetrating rays was not aimed at in these experiments, the results given by the two methods of determining the reduction factor which are detailed below are close enough for the purpose in view.

(I) Calculation of the capacity C from the geometry of the electrode and cage, coupled with a direct determination of the potential difference v which caused a movement of one scale division. The product Cv then gives the quantity sensitivity, for the change in C which arises from the movement of the leaf during an observation is insignificant. Taking account of the fact that the mirror and the bridge which holds its hinges project slightly from the electrode the value of C has been determined as 0.42 ± 0.03 cm. To obtain v the usual large charging contact was replaced by a long thin wire arranged to touch the top of the electrode and so to cause a minimum of disturbance of the distribution of charge. This value of v was several times altered in the course of the work by using the instrument at different tilts.* The maximum

* The value of v did not vary by more than 1 per cent. over the portion of the scale used in the observations.

value employed, 0.04 volts per millimetre, corresponded to a quantity sensitivity of 5.6×10^{-5} e.s.u. per millimetre, or, dividing by the electronic charge, 1.17×10^6 ions per millimetre.

(II) Calibration with a standard γ -ray source at a known distance, using Eve's number, N , to calculate the ionisation per cubic centimetre, and allowing for absorption in the walls of the vessel and the air. This method involves uncertainties in the exact value of N and in the degree of saturation attained in the chamber. A number of measurements were made with a radium standard (4.72 mgm.) at a distance of 4 metres. Taking N as 4.10×10^9 , and the degree of saturation as 100 per cent., it was found by this method, that in these experiments the quantity sensitivity was 2.10×10^6 ions per millimetre.

The voltage sensitivity was at the same time determined as 1/17 volts per millimetre, so that the quantity sensitivity calculated by method (I) was 1.73×10^6 ions per millimetre.

The α -particle jumps themselves give some information on the question of quantity sensitivity, for the total ionisations caused by α -particles of various origins are known. Here, however, the uncertainty is in the degree of saturation attained in the chamber, where the radial electric field varies from 1200 volts per centimetre at the electrode, to 3.6 volts per centimetre at the boundary. Thus the degree of saturation and the effect caused by an α -particle depend very much upon the position of its track. It can be shown from Moulin's* results that the most favourable conditions for a radium C' α -particle of range, in CO_2 at 62.3 cm. pressure, 5.4 cm., will arise if it just grazes the central electrode at the middle of its range, when an average degree of saturation of about 75 per cent. will be attained. The following table exhibits the distribution of 535 α -particle jumps, observed under conditions of constant sensitivity, in respect of their size. The first column gives the range of each group of jumps, and the second the number found to lie within each group. In the last two columns the jumps which would be caused by the various possible α -particle disintegrations are given and placed opposite the groups into which they would fall. For these calculations a degree of saturation of 65 per cent. has been assumed and a quantity sensitivity of 1.63×10^6 ions per millimetre, determined by method (I) for the value of v (1/18 volt) which was used.

The distribution of the jumps fits reasonably well with the presumed origin of the particles. The large number of small jumps is due to α -rays whose tracks are only partly within the cage. Only 14 jumps, 3 per cent. of the whole

* 'C. R.,' vol. 148, p. 1757 (1909).

Table II.—Distribution of α -particle Jumps.

Jumps between	Number.	Possible origin (65 per cent. saturation).
0.05 and 0.25 mm.	47	
0.25 and 0.45 mm.	65	
0.45 and 0.65 mm.	57	Ra Em 0.61 mm.
0.65 and 0.85 mm.	78	Ra A 0.66 mm.
0.85 and 1.05 mm.	128	Ra C' 0.87 mm.
1.05 and 1.25 mm.	83	Th C' 1.00 mm.
1.25 and 1.45 mm.	37	
1.45 and 1.65 mm.	26	{ Th Em + Th A 1.46 mm.
1.65 and 1.85 mm.	10	Ac Em + Ac A 1.59 mm.
1.85 and 2.05 mm.	1	
2.05 and 2.25 mm.	2	
2.25 and 2.45 mm.	1	
>2.45 mm.	0	

number, give larger effects than are accounted for in column 3, and some of these arise from observational error in counting two close jumps as one. The double disintegration, Th Em followed by Th A, was fairly often observed as a pair of jumps separated by a time interval of the order of 1/5th of a second, and usually recorded as a single jump.

§ 6. *Fluctuations in the Intensity of the Penetrating Rays.*

In connection with Table I, it has already been pointed out that the method of measurement allowed of the determination of the ionisation produced during single minutes. For minutes during which no α -particles appeared this could certainly be done with an error of less than 5 per cent., and yet it was found that fluctuations amounting to more than 20 per cent. of the mean value were occasionally observed. These must be ascribed to probability variations in the number of ionising particles.

If Z is the average number of particles arriving in a given interval of time, the mean relative fluctuation ϵ' in the ionisation is $1/\sqrt{Z}$,* supposing that each particle contributes equally to the total ionisation. In the present case this condition is not fulfilled, since the ionisation chamber is not spherical and the rays are incident at various angles. The value of ϵ' therefore becomes $\sqrt{1 + \epsilon''^2}/\sqrt{Z}$, where ϵ'' is the mean relative fluctuation in the effect of a single particle.*

To examine this point, I have taken the individual minute readings from two series of fine-weather observations, made under conditions of high sensitivity

* Meyer and von Schweidler, "Radioaktivität," 2nd ed., p. 44.

and excluding minutes disturbed by α -particles. The relevant data are shown in the following table, in which the third column is obtained by multiplying the figures in the second by $2.28/2.58$ to eliminate the residual ionisation (§ 8).

Table III.—Fluctuations in Intensity during Single Minutes.

Number of single minute observations.	Mean movement in 1 minute.		Mean fluctuation.	Z (calculated).
	Observed.	Corrected.		
	mm.	mm.	mm.	
95	3.59	3.16	0.22	206
43	4.10	3.64	0.26	197

The value of Z in the last column has been calculated assuming ϵ'' to be zero. The individual observations are found to fit fairly well to the Bateman* formula $\frac{Z^n}{n!} e^{-Z}$ for the probability of the appearance of n -particles in 1 minute.

taking Z to be 200. Estimating ϵ'' to be 0.40 would raise the value of Z to 230 particles per minute, and this would mean that the rays fell upon the ionisation chamber at the rate of between 0.01 and 0.02 particles per square centimetre per second. Bothe and Kolhörster† have given 0.01 for the value of this quantity at sea-level and it should be about double at this height.

The importance of this discussion for the present experiments lies in the fact that fine-weather fluctuations in the ionisation are to be expected even when a 10-minute interval is chosen as the period of observation, while the detection of small thunder-storm effects of short duration is subject to difficulties which could only be overcome by the use of much larger ionisation vessels.

§ 7. Variation in Fine-weather Intensity with Time of Day and with Pressure.

It is of some importance to enquire whether the observations reveal any variation in the fine-weather intensity with time of day, not only because such variations might affect the discussion of thunder-storm observations, which were generally made in the early afternoon, but also because of the possibility that geographical position might have some influence upon the variation. Unfortunately, continuous observations by the method described could not be made over long periods of time owing to the strain involved in watching for

* 'Phil. Mag.,' vol. 20, p. 698 (1910).

† 'Z. Physik,' vol. 56, p. 772 (1929).

α -particles and readings had to be taken by an easier but less accurate method during the few days on which no thunder-storms occurred. The instrument was allowed to run for an hour at a time over the same portion of the scale, about 200 mm. long, without observation of the effects of α -particles. The results are shown in fig. 4 and fall into two sets: those made from 6 p.m. to 11 a.m. (Greenwich mean time) on February 3 and 4 are marked with crosses, and those made from 8 a.m. to 11 p.m. on February 6 with circles. The α -particle effect of 0.4 mm. per minute and the residual β - and γ -ray ionisation effect (§ 8) of 0.3 mm. per minute, have not been subtracted from the readings.

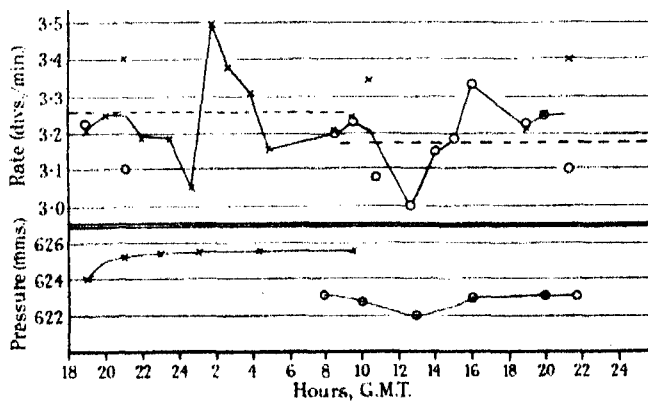


FIG. 4.

The mean rate of fall for the first set of 13-hour observations is 3.26 mm. per minute with a mean fluctuation of 0.1 mm. per minute or 6.0 mm. per hour. For the second set of 10 observations the mean rate of fall is 3.17 mm. per minute with a mean fluctuation of 4.2 mm. in the hour values. Since it is known from direct measurement (§ 4) that the average number of α -particles per hour was 25 and the average effect of each about 1.0 mm., ordinary probability variations in the number of α -particles would have given rise to a mean fluctuation of 5.0 mm. in the hour values. Though the observed variations with time of day may thus be ascribed to α -particle effects and in any case do not amount to more than 6 per cent. of the mean, the difference between the averages of the night and day sets may have a more fundamental cause. For the present purpose, however, it may be concluded that during the day-time and using the more accurate method of observation by which α -particle effects are eliminated, no large variations of the intensity of the radiation with time of day are to be expected.

The possible effect of a change in atmospheric pressure has also to be borne

in mind in discussing changes in the intensity of the rays during thunderstorms. At this height, the results of Steinke* indicate that it should be of the order of 6 per cent. per centimetre of Hg change in pressure, increase of pressure causing a decrease in the ionisation. Variations of pressure of as much as 0.5 cm. are rare at Johannesburg and there was thus no opportunity of obtaining information on the "barometer-effect." The pressures corresponding to the two sets of readings just discussed are shown in fig. 4, but the expected 1 per cent. pressure effect is in the opposite direction to the 3 per cent. difference already noticed. The pressure during a thunder-storm never altered by more than 0.25 mm. from its fairly steady value before and afterwards so that a change in the intensity of the radiation of less than 1.5 per cent. can be ascribed to this cause. In most storms the pressure change was inappreciable.

§ 8. *The Local Radiation Effect and the Fine Weather Ionisation.*

The apparatus was installed in an upper room in a brick building rather than in a hut because previous experience had shown that it required special care to work it satisfactorily during a thunder-storm when sudden changes of temperature, violent winds, and vibration due to hail and rain on the roof tend to upset the movement of the leaf. The brick walls, however, introduce a double complication; they reduce the intensity of the penetrating radiation by shielding the instrument, and they themselves emit a γ -radiation. From most of this local radiation the apparatus was satisfactorily screened by the rampart of iron blocks with a half-angular aperture, ϕ , of 66° , but from about half-way up each wall to the top of the wall ($\phi = 45^\circ$) there was no screening other than that provided by the iron walls of the ionisation vessel itself.

To get an estimate of the order of magnitude of the effect due to these rays, we may refer to some observations made by Steinke† at Königsberg, in a brick building with walls 25 cm. thick and using an ionisation chamber with iron walls of the same thickness as in my instrument. The angle ϕ for the tops of the walls was 52° and the effect of the roof negligible. It can be found from his curves that the effect of the local radiation between 50° and 70° amounted to about 0.32 J. The conditions in the present experiments were so similar that a value of 0.30 ± 0.10 J is not likely to be far out. Since the ionisation arising from α -particles inside the vessel is allowed for in the measurements, and that of β - and γ -rays from the walls of the vessel is of quite a different

* 'Z. Physik,' vol. 47, p. 682 (1928).

† Steinke (*loc. cit.*), p. 659; also 'Z. Physik,' vol. 42, p. 573 (1927).

order of magnitude, the above figure represents the total residual effect to be subtracted from the observed ionisation to get that arising from the penetrating radiation.

Forty-three 10-minute observations were made during fine weather at the same sensitivity, determined by method (I) as 1.66×10^5 ions per millimetre. The average rate of movement was found to be 2.96 mm. per minute. Reducing from CO₂ at 20° C. and 62.3 cm. pressure to air at N.T.P., the total fine-weather ionisation is found to be 2.58 J. After subtraction of the residual effect, 0.30 J, this gives a value of 2.28 J for the ionisation due to the penetrating rays.

This result may be compared with observations made by Steinke* under similar conditions of screening and height above sea-level.

Davos (Steinke).		Johannesburg.	
[1600 m.]		[1780 m.]	
0° to 45°	Unscreened	0° to 45°	Unscreened
50° to 90°	12 cm. Fe	45° to 66°	Brick equivalent to 8 cm. of Fe
66° to 90°		66° to 90°	Brick plus 15 cm. Fe
J _H	2.59 ions c.c. sec.	J _H	2.28 ions c.c. sec.

From the work of Millikan† in North and South America, it seems that geographical position does not markedly affect the intensity of the penetrating rays, so that the approximate agreement of these results supports the estimated value of 0.30 J for the local radiation effect.

§ 9. Thunder-storm Observations.

The runaway electrons, which it was hoped to observe below the most active portions of the thunder-clouds, could only be expected to occur during periods of intense negative field, such as prevail just before the passage of lightning discharges. They should have shown themselves by a momentary increase in the rate of movement of the spot of light, reaching a maximum at the instant that the flash took place.

A very careful and continuous watch was therefore kept upon the movement of the spot for any such unusual changes in rate. In addition, the ordinary minute and 10-minute readings were made and these could be compared with the fine-weather values.

* E. Steinke (*loc. cit.*), p. 666.

† R. Millikan, 'Phys. Rev.', vol. 31, p. 163 (1928).

(a) *Momentary Changes*.—Nine thunder-storms passed directly overhead, all giving rise for most of the time to strong negative fields at the ground, and amounting in all to more than 3 hours of overhead lightning of the most active character. Three other storms passed nearly overhead and gave rise to similar fields. There were at least two close discharges from the cloud to the ground, one at 250 metres and the other at 400 metres distance. Details of these storms are given in Table IV below.

In spite of these favourable conditions, the evidence for momentary effects is very meagre. The only unusual changes in rate were two sudden jumps, indistinguishable from the effects of α -particles, 1 and 2 mm. in size respectively, which were apparently simultaneous with the occurrence of two close lightning discharges which took place within the cloud. Both of these jumps were observed during the same storm, No. 10, which also produced the closer of the two flashes to ground which have been mentioned. These ground discharges were certainly not accompanied by any unusual changes in the ionisation.

If these two jumps had any real significance in this connection, one would expect to find an increase in the number of sudden jumps ascribed to α -particles, during periods of strong negative field, but this is not the case, for the $\Sigma\alpha'$ observations during thunder-storms were quite normal.

(b) *One-minute Observations*.—It has been pointed out in § 6 that probability fluctuations in the number of ionising particles affect the 1-minute readings rather badly. These have been examined, however, to see whether any of them show increases which could be ascribed to runaway electrons. The later storms only are available for this test, which has been made by picking out those 1-minute readings which exceed the mean value during fine-weather by more than 20 per cent. The results are shown below.

Strong -ve field.	+ve or no field.	1-minute values $> 1.20 \times$ fine-weather mean.
minutes 210	minutes —	2 (1.22, 1.21)
—	470	7 (1.30, 1.21, 1.20, 1.27, 1.26, 1.22, 1.33)

These figures show no effect of the kind sought for. The strongest negative fields were not associated with the two 1-minute values given in the first line.

(c) *Ten-minute Observations*.—Two or three fine-weather measurements were made every morning in order to be able to compare fine-weather observations

with those made when thunder-storms were at various distances. During the storms, which occurred in the afternoons or evenings, as many observations as possible were made and several more fine-weather measurements were always taken after the storms had passed far away. The quantity measured was the average rate of movement per minute during 10 minutes, corrected for the effects of α -particles, that is $(D - \Sigma\alpha)/10$.

Observations were made in this manner upon 17 of the 22 thunder-storms which occurred. Nine of the storms examined in this way came within a distance of 5 km., and seven passed directly overhead.

The sensitivity of the apparatus was altered several times during the course of the work and the mean of the fine-weather readings, from 5 to 21 in number, for each sensitivity has been taken as unity in order to present all the results on the same scale. Thus every reading, in both fine and thundery weather, has been expressed in terms of the corresponding fine-weather mean.

The collected results are shown in fig. 5, each point of which represents a single 10-minute reading. The results have been assembled in five classes,

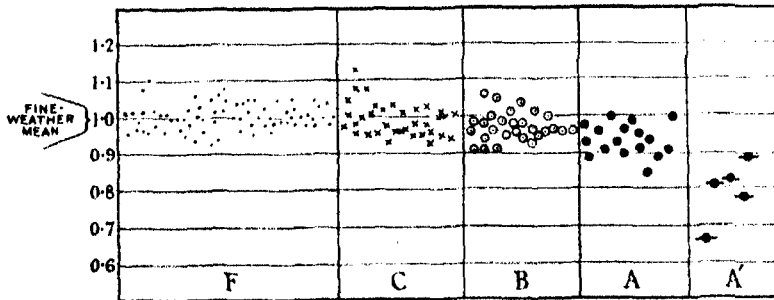


FIG. 5.

of which the first (F), contains the fine-weather measurements. These exhibit a spread, due in the main to the probability variations discussed in § 6. The C group shows the measurements made when thunder-storms were more than 10 km. away, the B group those for storms between 5 and 10 km., and the A and A' groups both refer to measurements made when the storms were less than 5 km. away. These results show that there is a definite decrease in the ionisation as the cloud approaches, which reaches its maximum in the case of the overhead storms in group A'.

The distinction between A and A' storms is based upon the nature of the electric field observed below them; in the case of the A storms this was predominately negative, in that of the A' storms it was predominately positive.

At Johannesburg, as elsewhere in South Africa, the sign of the "steady" field (E_s), which prevails just before the cloud discharges, is almost always negative. The field is, however, constantly changing; lightning discharges reduce it from E_s to zero or even to a large positive value, after which it recovers in a manner and at a rate which varies with the storm. In correlating the reduction in the ionisation with the electrical state of the cloud, the average value of the field (E_{av}), is likely to be more significant than E_s , and this is clearly brought out in the figure. The A storms were those for which E_{av} was negative and they showed only moderate reductions on the whole, sometimes no reduction at all. The A' storms were those in which E_{av} was positive, a large positive change of field being followed by slow recovery to a small positive or negative value of E_s , on attaining which a discharge giving another large positive change occurred. The reductions observed with these storms were much larger, but unfortunately such storms were infrequent.

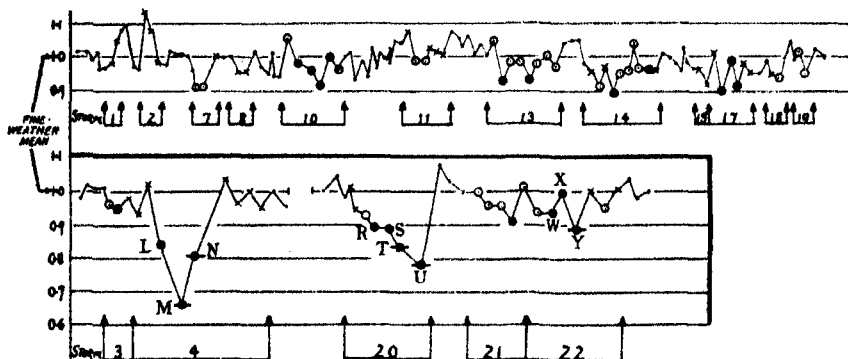


FIG. 6.

Fig. 6 shows the observations for each storm separately; the unit is again the fine-weather mean and the symbols used to distinguish measurements made at different distances and under different electric fields are the same as in fig. 5. Each storm is indicated by its serial number below the corresponding observations and information on the nature of the storms is summarised in Table IV. All the storms in the first line and storms 3 and 21 in the second line of this figure were of type A. The three other storms in the second line were of type A' for part of the time, and further information about them is given below.

Storm 4.—This occurred before the point-discharge indicator had been set up. An electrometer recording the potential gradient photographically showed that E_{av} was negative during observation L and became strongly positive,

greater than the limit of the instrument, 5000 volts per metre, during M and N.

Storm 20.—This was a very violent hail-storm. During observation R, E_{av} had a fairly large negative value increasing from -1.5 to -9 cm. on the galvanometer scale as the storm approached from 6 to 4 km. S was a short observation immediately following R and constituted the first 6 minutes of a 13-minute run of which T formed the last 7 minutes. During S, E_{av} changed from a large negative value (galvanometer deflection -5 cm.) to a large positive one ($+10$ cm.), at which point T begins. Throughout observation T heavy hail was falling and E_{av} was strongly positive ($+10$ to $+30$ cm.). The actual positive changes of field were exceptionally numerous and large. There is little doubt that the storm passed directly overhead, though the noise of the hail prevented measurements of the lightning-thunder interval. Observation U was made 4 minutes after observation T when the hail had ceased; the cloud was still quite near (7 seconds) and E_{av} was positive ($+4$ cm.).

Storm 22.—This was also a violent storm. During observation W the field was strongly negative and the storm distant from 3.5 to 5 km. During X, E_{av} was again negative; the storm was now right overhead with a thunder interval of 5 seconds and gave rise to 31 positive and 2 negative changes of field in 10 minutes. Y is the first 7 minutes of a run during which E_{av} became positive and a heavy fall of rain and hail took place. In the next 3 minutes

Table IV.—Thunder-storm Data.

Storm No.	Type.	E_s .	E_{av} .	Discharges per minute.	Nearest flash (secs.).		Remarks.
					In cloud.	To ground.	
3	A	-ve	-ve		overhead*		
4	A'	?	+ve		overhead*		
6	A	-ve	-ve		overhead*		
10	A	-ve	-ve	2	4	1.5	(a) Observations only.†
13	A	-ve	-ve	1	5		Active storm.
14	A	-ve	-ve	1 to 2	11		Mild storm.
16	A	-ve	-ve	1 to 2	6		Active storm.
17	A	-ve	-ve	1 to 2	5	2.0	(a) Observations only.†
			(big)				Active storm.
19	?	0	0	2	12		Very active.
20	A'	+ve	+ve	3 to 4	overhead*		Violent hail-storm.
			(big)				
22	A	-ve	-ve	2 to 3	5		Violent.
	and A'	and +ve	and +ve				

* No actual measurements of lightning-thunder interval.

† Observations for momentary effects only.

the storm decreased in activity and moved away fast, while the rate of movement of the spot rose to normal.

The following summary may be made of the results described in this section :

- (1) Nosignificant momentary effects have been observed which can be ascribed to runaway electrons.
- (2) Thunderstorms at distances greater than 10 km. caused no special changes in the ionisation.*
- (3) Overhead thunder-storms produced a reduction in the ionisation and therefore succeeded in stopping some of the ionising particles.
- (4) The reduction was much greater in the case of A' than of A type storms.

In support of (1), mention may be made of some observations carried out a year previously at Somerset East with a similar but less sensitive apparatus. Six active storms passed overhead and the movement of the leaf was watched for momentary effects but none were observed, although strong negative fields prevailed for several hours in all. The residual ionisation, about 13 J, was too large for the reduction effect here observed to be detected with certainty.

§ 10. *Discussion of Results.*

The measurements shown in figs. 5 and 6 refer to the total ionisation within the vessel, but the reduction is clearly in the ionisation due to the penetrating rays alone, and can be obtained in terms of this by multiplying the observed effect by $2.58/2.28$, using the value given in § 8 for the effect of the local radiation. The reduction produced by the A storms thus varies between 0 and 10 per cent. of the average fine-weather ionisation due to the penetrating rays, while that produced by the A' storms varies between 12 and 39 per cent.

These thunderstorms must be considered to stop the ionising particles as a charged grid or a pair of such grids, one above the other, might stop them, for the effect cannot be ascribed to the water carried in the cloud, the effective thickness of which is certainly less than 10 cm.

The observations of Steinke (*loc. cit.*) at Davos suggest that approximately half the ionisation at this height is caused by rays included within a vertical cone of half-angle 45° . Since it is unlikely that the active portion of an overhead storm could cover as large a solid angle as this, a reduction or screening effect of less than 50 per cent. would be expected even if the cloud were continuously active in stopping the rays. The reductions observed in the case of

* Mention has already been made in § 4 of the fact that the accuracy of observation was improved after storm 9. The single high C value in storm 2 is not considered significant.

the A' storms are therefore surprisingly large and suggest that they are for most of the time able to stop most of the particles which would otherwise pass through them.

Any particle which is stopped by the fields produced by a thunder-cloud either inside or outside the cloud itself, must have an energy less than that acquired by falling through the potential difference between the poles of the cloud. This quantity has recently been shown by C. T. R. Wilson* to be of the order of 10^9 volts, perhaps sometimes as great as $5 \cdot 10^9$ volts, and certainly less than 10^{10} volts. The closeness of the screening effect caused by the A' storms to the maximum which could be expected from the geometry of the cloud, therefore indicates that most of the ionising particles have an energy less than 5×10^9 volts. This does not necessarily imply that the primary rays themselves are charged particles, for an ultra-gamma radiation, of the characteristics suggested by Millikan,† produces all its ionising effects by means of recoil electrons arising from Compton scattering, and if robbed of these by retarding fields may be unable to recover others before reaching the ground.

Extrapolations of β - and γ -ray formulæ have been widely used to determine the energies of the penetrating rays from ionisation-depth curves. Except perhaps in the case of Regener's‡ results at great depths, which if interpreted as due to β -particles require energies greater than 10^{10} volts, the energies so derived all lie below the upper limit here found.

The absence of any large runaway electron effect below these storms is rather surprising, for a rough estimate shows that a considerable effect might have been expected, if the necessary fields had existed for a sufficient time and over a sufficient distance. A reasonable value, $1 \cdot 5 \times 10^{-16}$ curies per cubic centimetre, for the radioactive content of the air below the cloud implies the emission of 10 β -particles per cubic metre per second. At least one in four of these may be supposed to be emitted in such a direction that the field could cause it to gather energy.§ If the process were limited to the first 400 metres below the cloud, there would be one primary runaway electron produced per square centimetre per 10 seconds. The effect in the ionisation chamber, filled with CO_2 at a pressure of 62 cm., due to these alone would amount to 5.0 ions per cubic centimetre per second if we take the number of ions per centimetre

* 'J. Franklin Inst.,' vol. 208, p. 1 (1929).

† 'Phys. Rev.,' vol. 31, p. 921 (1928).

‡ 'Naturwiss,' vol. 17, p. 183 (1929).

§ Wilson, *loc. cit.*

of path in air to be 40. Thus the primary effect, if it existed for a single second, would produce a total of 1.3×10^4 ions within the chamber, enough to cause a change of 0.08 mm. in the position of the spot of light, and to increase the movement during a minute by 2.5 per cent. To this, however, must be added the effect of secondary electrons produced by collisions within the field with sufficient energy and in the right direction to be similarly accelerated. Recent measurements by Williams and Terroux* have shown that primary particles of velocities ranging from 0.6 c. to 0.97 c., eject about two such secondary electrons of energy greater than 20,000 volts in passing through a metre of oxygen at N.T.P. The number of secondaries will be smaller for still higher velocities, but it is clear that their contribution is likely to be very large. With the action of these secondary rays added to that of the primary runaway electrons, the effect should have been easily detectable even if it had lasted for, but a fraction of a second and if the fields had been far more limited in extent than has been assumed above.

Although Wilson (*loc. cit.*) has recently given reasons for supposing that the critical sparking field in the presence of water-drops is 10,000 volts per centimetre, a third of the usual value, this does not seem to invalidate the argument for the runaway electron effect, which may be briefly restated as follows: The average numbers of ions produced in the first centimetre of their path in air by the β -rays from radium B and C have been found by Geiger and Kovarik† to be 133 and 108 respectively. Taking 30 e.-volts as the average energy spent in an ionisation act, a field of 10,000 volts per centimetre should enable more than half these particles to gain energy at the rate of at least 6000 volts per centimetre in the first centimetre, increasing afterwards to about 9000 volts per centimetre as they gather speed. After traversing the first metre their energies would be of the order of 10^6 e.-volts and they would continue to gain energy until the field fell to 1000 volts per centimetre. The usual range-energy formula‡ indicates that to enable them to traverse 1.5 km. of air and to enter the ionisation vessel, such runaway electrons need only obtain 1.5×10^8 e.-volts from the field. This would require a field of 10,000 volts per centimetre to extend over about 160 metres or one of 5000 volts per centimetre to extend over 400 metres. Although the positive ions due to point discharge limit the field at the ground to about 200 volts per centimetre,§ it seems unlikely that

* 'Proc. Roy. Soc.' A, vol. 126, p. 305 (1930).

† 'Phil. Mag.', vol. 22, p. 604 (1911).

‡ Varder, 'Phil. Mag.', vol. 29, p. 725 (1915); Schonland, 'Proc. Roy. Soc.', A, vol. 108, p. 203 (1925).

§ Schonland, *loc. cit.*

they could restrict the strong field below the cloud-base to a very small region. That fields approaching the sparking value existed fairly often below the cloud is evidenced by the frequent passage of discharges carrying a negative charge from the base of the cloud to the ground.

While, therefore, it is not possible to be sure that the requisite conditions for the production of runaway electrons existed below these clouds, the arguments given suggest that it is more reasonable to seek for the explanation of their absence in some action which prevents them from reaching the ground. This possibility was foreseen by Wilson, who drew attention to the fact that once in every 500 metres a runaway electron would approach a nitrogen or oxygen nucleus within a distance (3×10^{-13} cm.) at which there is reason to believe the inverse square law of force to break down.* He suggested that the result of such a collision might be disastrous to the β -particle and involve the radiation of a γ -ray quantum, or a nuclear disintegration. Williams and Terroux (*loc. cit.*) have recently drawn attention to a fast β -ray track which appears to show such a sudden stoppage and the emission of the energy as radiation. After travelling 500 metres in a field of the critical sparking value a runaway electron would have acquired about 5×10^8 e.-volts of energy and while nothing can usefully be said about the probable efficiency of the conversion of this into radiation, the absence of any significant increase in the ionisation suggests that the efficiency is very low.

The difference between the screening effect of A and A' storms suggests at first sight that some ionisation due either directly or indirectly to runaway electrons actually occurs. One might suppose that both were equally effective in screening and that the A storms, which give rise to negative fields below, produce runaway electrons which may or may not be converted into ultra-gamma radiation before reaching the ground. But against this it can be urged that the A storms showed neither the momentary effects nor the abnormally high 1- or 10-minute values to be expected, and that storms so evidently different in electrical constitution would be likely to behave differently in stopping the penetrating rays. A brief suggestion as to the real origin of this differential screening effect may be ventured, bearing in mind that only three storms occurred which can be classed as of type A' and that the information about two of these is scanty.

The A and A' storms seemed to be similar in one respect; in both cases the changes of field due to lightning discharges were predominantly negative at a distance and predominantly positive when overhead. Thus in both types,

* Bieler, 'Proc. Roy. Soc.,' A, vol. 105, p. 434 (1920).

the most frequent discharges involved a downward movement of positive electricity and the most powerful fields were those between an upper positive and a lower negative pole. The passage of a flash did not, however, completely discharge the cloud, for in general a charge of either positive or negative sign remained, giving rise to a strong field below and presumably above the cloud. This excess of charge of one sign is to be ascribed to a difference in the rate of dissipation of the charges on the two poles. In the case of the A' storms it was large and positive, in that of the A storms it was usually small and negative. It seems natural to ascribe the differential screening effect to this difference in the sign of the excess charge on the cloud and to conclude that an excess positive charge is far more effective than a negative one.

This conclusion has an interesting bearing upon the nature of the penetrating rays. If we suppose that these consist of charged particles, it is evident in the first place that the nature of the field below the cloud can have no influence upon the screening effect, for if they can pass through the base of the cloud, the remainder of their journey can only result in their arrival at the ground with the same energy that they would have had if the cloud had not been present. The field below merely subtracts from or adds to them the extra energy already gained or lost in the fields above and within the cloud. One would naturally expect the stoppage of the particles to take place within the cloud, between the poles of which the largest potential difference exists, but such a view offers no explanation of the difference in the stopping power of A and A' storms, for both types are similar in respect of their internal fields.

There remains the field above the cloud, which, in the case of a thunder-cloud of positive polarity with equal charges, is directed upwards and could only effect a stoppage of positively charged particles. In an A' storm this field is enhanced by the excess positive charge, but in an A storm it is weakened or reversed by the excess negative charge. In the former the potential of the upper positive pole may be of the order of 10^9 volts, and in the latter it may differ but little from that of the upper atmosphere, 10^6 volts. It is therefore suggested that the superior stopping power of A' storms may be explained if the radiation consists of positively charged particles and the stoppage takes place above the thunder-cloud.

A second possibility, however, is that the radiation is of ultra-gamma type and that its Compton electrons are removed by the fields within both A and A' storms. Here the differential screening effect which could not arise in the case of a pure β -radiation may have its origin in connection with the regeneration of these electrons by Compton scattering during the passage of the radiation

through the 1.5 km. of air which separate the base of the cloud from the ground. In the absence of any field below the cloud this regeneration would be approximately completed after the waves had travelled a distance equal to the average range R of the electrons associated with them. If D is the distance between the base of the cloud and the ground, the fraction of the electron complement regained would be D/R , which, of course, has a maximum value of 1.0. The values of R for the three components found by Millikan* at this height can be calculated from the Klein-Nishina formulæ† to be 2.9, 1.4, and 0.30 km., giving values of D/R which are equal to 0.5, 1.0 and 1.0, the two softer components being able to regenerate their ionising electrons completely. The fractional contributions of the three components to the total intensity were found by Millikan to be 0.28, 0.38, and 0.34, respectively, so that the fraction recovered should amount to $0.14 + 0.38 + 0.34$ or 0.86 of that lost within the cloud. If we suppose as before that only one-half of the radiation is subject to this screening action, a maximum reduction of 7 per cent. is all that could be expected. Consideration of the degraded,‡ once or more times scattered, radiation which accompanies the main beam, shows that the process of recovery would in reality be still more nearly complete.

This argument supposes that there is no field below the cloud, but actually the fields which exist below A and A' storms will modify the regenerative process and in opposite ways. The strong negative field below an A storm will assist regeneration by increasing the ranges of recoil electrons which would not otherwise enter the ionisation vessel. The positive field below an A' storm on the other hand will have the reverse effect and one could anticipate a complete absence of regeneration in the stronger parts of the field. No appreciable regeneration can take place within the 1 cm. top of the electroscope, for this is equivalent in electron content to only 50 metres of air. Thus the differential screening effect could easily arise if the radiation were of ultra-gamma type. The fact that small reductions were observed under the A storms is some evidence against this hypothesis as to the nature of the radiation, but it is possible that they arose during periods when the field below the cloud was positive.

If the experiment of Bothe and Kolhorster (*loc. cit.*) can be taken as establishing the corpuscular nature of the rays, this argument suggests that they are positively charged. It should be possible to carry the present experiments

* Millikan, *loc. cit.*

† 'Z. Physik,' vol. 52, p. 853 (1929).

‡ Gray, 'Proc. Roy. Soc.,' A, vol. 122, p. 663 (1929).

a stage further, by placing a sufficiently large thickness of iron above the ionisation vessel to ensure that complete regeneration could take place. If a reduction was still observed under these conditions, it would imply that the primary radiation was corpuscular.

To sum up this discussion, the screening effect sets an upper limit of 5×10^6 volts to the energy of most of the quanta or corpuscles which make up the penetrating radiation. The differential screening effect suggests that the primary radiation consists either of positive particles or ultra-gamma quanta. The absence of a runaway electron effect below the clouds is considered to arise from stoppage of the accelerated particles by direct nuclear collisions.

As far as experiments below a thunder-cloud can go, the evidence here discussed is against the view that thunder-clouds are the main source of the penetrating radiation, but it must be pointed out that Wilson's original suggestion refers to the upward moving particles produced within the cloud where the fields are almost certainly of the necessary magnitude and extent. The suggestion only falls away if nuclear stoppage is the correct explanation of the absence of any downward-moving particles.

I wish to thank Mr. J. Linton for his valuable aid in the construction of the ionisation vessel, Prof. Paine and the staff of the Physics Department of the University of the Witwatersrand for many kindnesses, Mr. E. L. Halliday for the use of information obtained by him on the question of cloud polarity, and my wife for acting as the second observer. I have also to make grateful acknowledgment of financial assistance from the South African Research Grant Board and the Research Fund of the University of Capetown, and of the encouragement and advice of Prof. C. T. R. Wilson, who suggested this investigation.

Summary.

A description is given of an ionisation-electroscope suitable for the measurement of small and rapid changes in the intensity of the penetrating rays. Measurements with this instrument have been made at Johannesburg in both fine and thundery weather, with the following results:—

(1) The fine weather ionisation showed fluctuations which can be attributed to probability variations in the number of ionising particles and indicates that from 0.01 to 0.02 particles occurred per square centimetre per second at this height.

(2) A search was made for beams of downward-moving "runaway" electrons in the negative fields below thunder-clouds. Despite very favourable con

ditions, no such electrons could be detected, and it is suggested that they are stopped by direct nuclear collisions before reaching the ground.

(3) It was found that a reduction in the intensity of the radiation took place when active thunder-clouds were overhead. This was the only thunder-storm effect observed.

(4) This reduction was greatest under those storms for which there was evidence that the upper positive charge was in excess, a result which suggests that the primary penetrating radiation is not of β -ray type but consists either of positively charged particles or of ultra-gamma quanta.

Secondary Electronic Emissions from Metal Foils and Animal Tissues.

By W. V. MAYNEORD, M.Sc.

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Introduction.

The measurement of penetrating X- and γ -rays by means of an ionisation chamber has been the subject of a large number of experimental and theoretical investigations, but still presents interesting problems. The ionisation current observed in any given case depends (among other factors) upon the material of which the ionisation chamber is constructed, and entirely fallacious estimates of the relative intensities of beams of X- and γ -rays of different wave-lengths may be obtained, unless the influence of this factor be kept in mind. The experiments described below are concerned with the relative sensitivity of small ionisation chambers lined with various metal foils and animal tissues, when irradiated by beams of X- and γ -rays of different mean wave-lengths. Animal tissues were included among the materials of which chambers have been constructed, since the results of X-ray measurements with such chambers are of importance in the consideration of the question of relative sensitivity of living tissues to various penetrating radiations.

The ionisation current observed in small closed ionisation chambers (volume 1 c.c. approximately) filled with air at atmospheric pressure is due to ionisation produced in the air itself by the primary radiation and also to secondary effects

due to β -radiation produced in the walls of the chamber. The latter appears of relatively greater importance in small chambers, until with chambers of the order of size contemplated, the primary effect becomes negligible for walls composed of heavy elements,* and the ionisation current is almost entirely determined by the secondary electronic emission from the wall. In view of the complexity of the effects occurring in such a chamber we cannot hope at the moment to construct an adequate theoretical treatment, but may proceed to discuss the problem as below, in the hope of obtaining at least qualitative agreement with the observations.

Theory.

Consider a beam of short wave-length X- or γ -radiation, wave-length λ and intensity I_0 , falling on a plane sheet of material (atomic number N and thickness d) forming the face of an ionisation chamber. The intensity I_x of the radiation penetrating to a depth x into the metal will be, neglecting secondary effects, $I_x = I_0 e^{-\mu x}$, where μ is the linear absorption coefficient of the radiation in N .

The energy absorbed per unit area in a thickness dx is evidently

$$\begin{aligned} E_x &= (\tau + \sigma_a) \cdot I_x dx \\ &= (\tau + \sigma_a) \cdot I_0 e^{-\mu x} \cdot dx, \end{aligned}$$

where τ = photoelectric absorption coefficient, σ_a = true absorption coefficient associated with Compton scattering.

Assume that the whole of the energy absorbed will be converted into β -ray kinetic energy, but will not, owing to scattering and absorption, reach the far side of the sheet. Let an amount E_x' reach the air in the ionisation chamber. Then, according to Wilson,†

$$E_x^2 - (E_x')^2 = a(d - x),$$

a being a constant.

Let r be the range of the secondary electrons in N . Then

$$E_x^2 = ar$$

and

$$\frac{E_x'}{E_x} = \left[\frac{r - d + x}{r} \right]^{1/2}.$$

* M. Bruzau, These. Univ. de Paris (1928), 'Ann. Physique,' vol. 11, p. 1.

† Wilson, 'Proc. Roy. Soc.,' A, vol. 104, p. 1 (1923).

Whence the total energy in the form of electronic motion reaching the air and causing ionisation on the far side of the sheet is

$$\int_0^d E_x' dx = \int_0^d (\tau + \sigma_a) \cdot I_0 e^{-\mu x} \cdot \left[\frac{r-d+x}{r} \right]^{1/2} \cdot dx.$$

Since the sheets in these experiments are in general very thin

$$e^{-\mu x} \simeq 1$$

and

$$\int_0^d E_x' dx = (\tau + \sigma_a) \cdot I_0 \cdot \frac{2}{3} e^{-\mu d} \cdot \frac{r^{3/2} - (r-d)^{3/2}}{r^{1/2}}.$$

A maximum is evidently obtained when $r = d$, and the secondary electronic emission is equal to $W = (\tau + \sigma_a) \cdot I_0 \cdot \frac{2}{3} r$. For greater thicknesses the value will fall off approximately as $e^{-\mu d}$.

Consider therefore two ionisation chambers of the same dimensions but having walls of thicknesses d_1 and d_2 respectively, densities ρ_1 and ρ_2 , and irradiated by radiations of wave-length λ . Then the ratio of the ionisation currents (assumed entirely due to secondary effects in the walls) produced in the two chambers will be

$$R = W_1/W_2 = \frac{\frac{KN_1^4}{A_1} \lambda^3 \rho_1 + \sigma_a}{K \frac{N_2^4}{A_2} \rho_2 + \sigma_a} \cdot \frac{r_1^{3/2} - (r_1 - d_1)^{3/2}}{r_2^{3/2} - (r_2 - d_2)^{3/2}} \cdot [r_2/r_1]^{1/2} \cdot e^{\mu(d_2 - \mu_1 d_1)},$$

since $\tau/\rho = K \cdot N^4/A \cdot \lambda^3$. K is a constant $= 1.37 \cdot 10^{-3}$, according to Richtmyer,* while A_1 and A_2 are the atomic weights of the elements concerned.

Using this equation we may calculate the relative ionisation currents to be expected in chambers having walls of various materials and of various thicknesses. Evidently if λ is very small, τ is negligible compared to σ_a and we have (if $r = d$ approximately and both are small)

$$W_1/W_2 = \sigma_{a_1}/\sigma_{a_2} \cdot r_1/r_2.$$

But the range $r \propto 1/\rho$ approximately and therefore, since $\sigma_a \propto \rho$,

$$W_1/W_2 \rightarrow 1$$

independently of the material. For γ -rays we find experimentally that the ratio for light elements tends towards unity.

For λ of medium value, say $0.3 \text{ \AA}$, σ_a is negligible and the ratio becomes

$$W_1/W_2 = N_1^4/A_1 \cdot A_2/N_2^4 \cdot e^{-\mu_1 d_1 + \mu_2 d_2} \propto [N_1/N_2]^2,$$

* Richtmyer, 'Phys. Rev.', vol. 18, p. 13 (1921).

a relationship shown experimentally by Fricke and Glasser* to be correct. Thus the ratio should apparently increase in this region of wave-lengths to values (for such elements as copper to carbon) of the order of 90. For long wave-lengths, μ_1 for the heavier element increases so that $e^{\mu_1 d_1 - \mu_2 d_2}$ becomes small and the value of the ratio again decreases. Thus we might expect a maximum in the region of medium wave-lengths. This has in fact been observed† and is confirmed below. The above theory holds, of course, only for monochromatic rays, plane sheets of metal and small thicknesses, neglect scattering of the primary rays in the walls and also the complexities of the reflection of the secondary rays of the faces of the ionisation chamber. While it cannot, therefore, be regarded as more than a qualitative suggestion, it appears to correspond essentially with the more complex experimental results.

Physical Basis of the Biological Action of X- and γ -rays.

In a number of fields of enquiry it is desired to measure the energy absorbed in a given small volume of an extended medium when the latter is traversed by a penetrating radiation. An interesting example is afforded by the measurement of the X- or γ -rays energy absorbed within animal, or more particularly human tissues, subjected to such radiations. Normally the energy is too small to be measured conveniently by its calorific effects and an ionisation measurement is resorted to. The results obtained must evidently depend on the construction of the ionisation chamber employed and it was thought worth while considering the physical aspects of this question in some detail. A similar problem has recently been attacked by Gray‡ in the case of the Millikan penetrating radiation. Consider a mass of animal tissues irradiated by X- or γ -rays. The energy absorbed in a small volume dV around any point P within the medium at which we wish to measure the effect, may be written

$$\sum \lambda_1 \lambda_2 \dots (\tau + \sigma_a) \cdot I_\lambda \cdot dV,$$

the summation being extended over the various wave-lengths present in the primary and scattered radiations that will reach P. If we replace the medium within dV by air, then the ionisation current in this air may, according to the theoretical considerations given above, be represented by a similar expression, and the ionisation current may therefore be regarded as a measure of the

* Fricke and Glasser, 'Fort. Geb. Röntgen,' vol. 33, p. 239 (1925).

† Kroenig and Friedrich, "The Principles of Physics and Biology of Radiation Therapy," p. 58 (1922); Fricke and Glasser, *loc. cit.*; Holthusen and Ascher, 'Acta Radiol.,' vol. 41, p. 27 (1927); Braun and Kustner, "Strahlen," vol. 32, p. 550 (1929).

‡ Gray, 'Proc. Roy. Soc.,' A, vol. 122, p. 647 (1929).

energy absorbed per unit volume by the medium, provided that the ionisation chamber has walls of the medium itself. One other assumption is required, namely, that the absorption in air of the secondary electrons emitted from the walls of the chamber should be proportional to their absorption in the medium. Thus the investigations of Gray show that if we consider an air cavity within a scattering medium, that the energy lost per unit volume by β -particles in the cavity is ρ times the energy lost by penetrating radiations per unit volume of the medium, ρ being the ratio of the lengths of path in air and in the medium, for which the energy loss of a β -particle is the same. The assumption that ρ is independent of the velocity of the β -particle was mentioned above. Since the effective atomic number of an animal tissue is approximately that of air (see below) the range of β -particles in air and the medium will be approximately inversely as the densities and the assumption probably justified.

It may be noted finally that if animal tissues have an effective atomic number greater than that of air, the energy absorbed at any point will be greater than appears from a measurement of ionisation current with a standard measuring instrument having "air equivalent" walls. The divergence will depend on the wave-length of the radiation. These conclusions are confirmed experimentally below.

Experimental Method.

In order to obviate as far as possible effects due to variation of output of sources of radiation, the apparatus shown in fig. 1 was constructed. It consists of two similar cylindrical ionisation chambers A and B, 3.85 cm. long and 1.25 cm. internal diameter, mounted side by side in an ebonite block covered with lead. The central rods of the ionisation chambers may be connected to the measuring instrument by rotation of the contact C, while the outer walls of the chambers are earthed via the aluminium foil which covers the ebonite block. The outer walls of the ionisation chambers consist of paper graphited on both sides to make it conducting. The central rods are

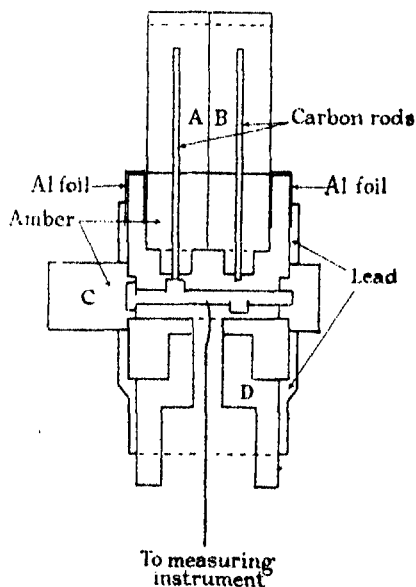


FIG. 1.

of carbon and screw into small pieces of brass covered with celluloid to avoid secondary radiation. The measuring instrument usually employed is a sensitive gold leaf electroscope charged positively to approximately 500 volts. Connection is made between the ionisation chamber and measuring instrument by means of an insulated cable, the central lead being carried on amber discs at intervals of about 2 cm.

The beams of rays employed were defined by means of lead stops near the X-ray tube so that only the ionisation chamber itself fell within the limits of the direct beam. Under these conditions the natural leak was small and in general negligible.

Specification of the Radiations.

As a fairly large region of wave-lengths has been employed, ranging from the γ -rays of radium to the unfiltered radiations from a Coolidge tube run at 60 KV., difficulty arises as to the most convenient way of representing the wave-length. In all earlier experiments the radiation has been defined in terms of an arbitrary "equivalent wave-length" λ_e obtained from a measurement of the absorption of the heterogeneous beam in 0.25 mm. copper and the use of standard absorption data.* It is not proposed to discuss the significance of this "equivalent wave-length," but the measurement is to be regarded as a purely arbitrary standard adopted because it is convenient over the range of radiations employed. Details of some of the radiations experimented with are given below.

Table I.

Peak voltage.	Filter.	λ_e .
		$\text{\AA}$
60	—	0.450
80	—	0.435
100	—	0.423
120	—	0.403
120	2.0 mm. Al	0.326
140	—	0.354
140	Metalix tube. 0.45 mm. Chrome-iron	0.255
160	—	0.244
180	—	0.230
200	—	0.220
160	Metalix tube. 0.45 mm. chrome-iron, +0.30 mm. Cu, +2.0 mm. Al	0.204
180	Metalix tube	0.185
200	—	0.172
γ -rays	1.0 mm. platinum	0.016

* Compton, "X-rays and electrons," p. 180.

Tests of the Small Paper Chamber.

Before proceeding with the experiments it is essential to ascertain whether the measurements made with a small ionisation chamber of graphited paper are independent of λ_c , that is whether its indications run parallel with those of a standard air gap ionisation chamber for different mean wave-lengths. In order to test this point the apparatus was set up so that a narrow beam of rays fell on to one of the ionisation chambers A or B, and also on a standard air gap chamber,* the aperture of the latter being arranged in such a position that the shadow of the small chamber fell just to one side of it, the total beam utilised being thus a narrow one in order to minimise errors due to differences in distribution of X-rays around the target with varying voltage and filtration.† Both standard chamber and small chamber were connected to the same gold-leaf instrument, the combined ionisation in the two chambers being observed. By lowering a lead cap (approximately 1 cm. thick) over the aperture of the standard, this could be "disconnected" without appreciably affecting the capacity of the system, or switching off the rays and risking the introduction of changes of output of the tube. The observed ionisation is now due to the small chamber only and in this way the ratio of the ionisation currents in the standard chamber and small chamber were determined for a number of peak voltages of the tube. The results are given in Table II. It was, however, shown by Behnken‡ that a chamber may appear to be free from errors when tested at various voltages and yet show appreciable errors when different filtrations are used. We have, therefore, carried out a series of experiments

Table II.

Peak voltage.	Ratio.
KV.	
60	1.48
80	1.40
100 (all unfiltered)	1.40
120	1.36
130	1.37
140	1.36
130 { 0 mm. Al	1.37
1 mm. Al	1.32
3 mm. Al	1.31
5 mm. Al	1.31
9 mm. Al	1.31

* Mayneord, 'Brit. J. Rad.,' p. 125 (1928).

† Coolidge and Kearsley, 'Amer. J. Roentgenology,' February, 1922.

‡ Behnken, 'Z. Tech. Physik.,' vol. 5, p. 3 (1924).

always using the same peak voltage (130 KV.) and varying the thickness of aluminium through which the rays pass before reaching the ionisation chambers.

It will be seen that there are no very large variations in the value of the ratio except for the least penetrating rays, and we have, therefore, used this paper ionisation chamber as our standard of reference in subsequent experiments. An ionisation chamber having still smaller deviations from an air chamber will be described later.

Experiments with Metallic Foils.

Using the apparatus previously described placed symmetrically in the beam of radiation, the metallic foils of various elements were inserted separately into one chamber so as to cover completely the inside surface, and the ratio of the ionisation currents in the two chambers found for various types of radiation. Experiments have been performed using foils of aluminium, copper, silver, gold, platinum, tin, and lead. Details of the foils are given below.

Table III.

Element.	Thickness.	Area.	Total weight.	Mass/Area.
	cm.	cm. ² .	gm.	gm./cm. ² .
Paper	0.035	14.0	0.647	0.0462
Al	0.006	13.23	0.0646	0.00488
Cu	0.0034	13.80	0.4182	0.0304
Ag	0.0022	13.84	0.3095	0.0224
Pt	0.0026	14.00	0.7941	0.0567
Sn	0.0023	13.80	0.2307	0.0167
Au	0.0021	14.00	0.5453	0.0390
Pb	0.0082	14.00	1.2934	0.0925

The experimental values of the ratios of the ionisation currents in the two chambers are plotted in a series of graphs (figs. 2 and 3). All experiments for which $\lambda_0 > 0.26 \text{ \AA.}$ were made with variable high tension applied to a standard Coolidge X-ray tube, the high voltage being obtained by the use of an induction coil (mechanical rectification of the secondary current). For the production of radiations having $\lambda_0 < 0.26$, a second X-ray set comprising an induction coil and valve rectifier was employed exciting a Philips Metalix Deep Therapy Type F tube. It will be seen from the graphs that in every case a maximum is observed in the ratio of the chambers. The position of this maximum lies in all cases in the region of medium equivalent wave-lengths, but the precise position depends on the element concerned and the thickness of the foil. The

elements of higher atomic number tend to have their maxima at shorter wave-lengths.

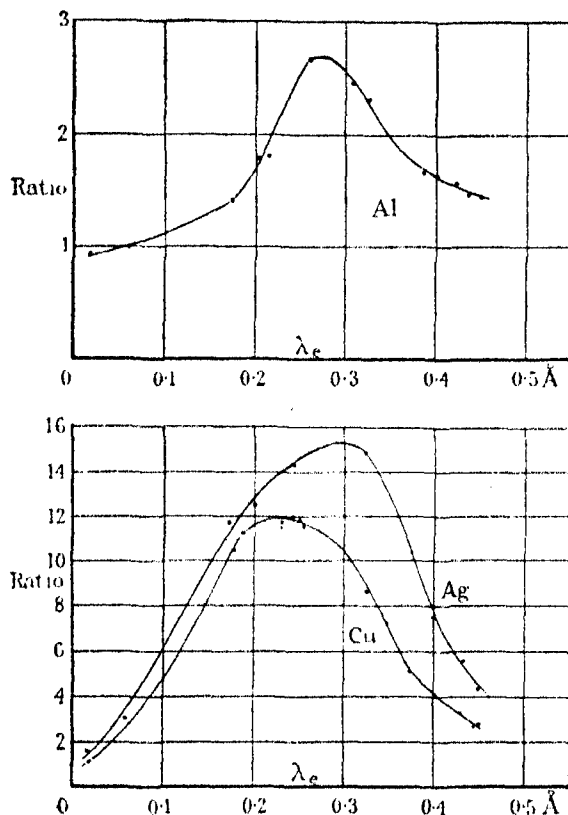


FIG. 2.

The results given in the curves for γ -rays ($\lambda_e = 0.016 \text{\AA}$.) were obtained by the use of 900 mg. Ra element in the form of RaSO_4 packed into approximately 400 platinum containers (wall thickness 0.5 mm.) varying in content from 50 mg. to 0.5 mg. Ra. These needles were placed in a lead box (wall thickness 4 cm.) having one side removed to allow the beam of rays to escape. A subsidiary filter of 1 mm. brass is inserted into the beam and the whole apparatus covered with approximately 1.0 cm. of a mixture of beeswax and sawdust. The ionisation chambers were at a distance of approximately 10 cm. from the radium.

The experimental values for γ -rays are given in Table IV. It is realised that the experimental results are complicated by the presence of β -rays. The original attempt was to reproduce therapeutic conditions.

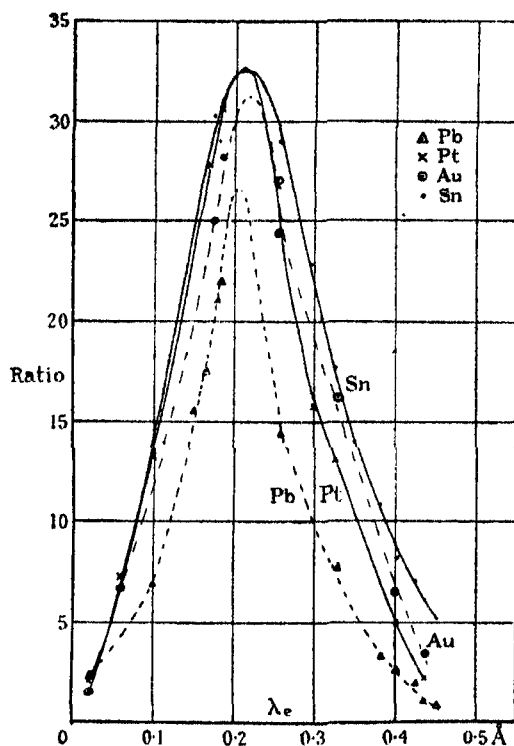


FIG. 3.

Table IV.

Material.	Ratio.	Material.	Ratio.
Paper	1.00	Sn	1.42
Al	0.90	Au	2.74
Cu	1.00	Pt	2.85
Ag	1.54	Pb	3.11

Although it seemed unlikely that exact agreement would be obtained, it seemed worth while attempting to verify the approximate formula previously given by inserting the appropriate values of τ , σ_a , ρ , r , d and μ and working out the ratios to be expected. Since the graphited paper behaves as an approximate air wall (deviating, however, slightly in the direction of too great atomic number) it has been treated as equivalent to an oxygen wall of the dimensions given. Values of μ were taken from the absorption data given

by Compton,* and the values of σ_a also worked out from his theory of scattering.† The values of τ may be obtained from the value of μ by subtraction of the value of the scattering coefficient σ_a appropriate to the wave-length.‡ The ranges of the β -particles cause most difficulty and were obtained as follows.

Consider a radiation of wave-length λ , frequency ν , incident upon an element of atomic number N . The energy of the photoelectrons emitted may be written

$$E_{KIN} = h\nu - E_{K, L, \dots},$$

where $E_{K, L, \dots}$ is the energy required to remove electrons from the K, L, ... level of N . Now

$$E_{KIN} = \frac{hc}{\lambda} \left[\frac{\lambda_{K, L, \dots} - \lambda}{\lambda_{K, L, \dots}} \right]$$

where $\lambda_{K, L, \dots}$ has its usual significance. Suppose that all the electrons are emitted from the level for which $\lambda_{K, L, \dots}$ is greater than λ , and nearest to it in absolute value. Then the range of the photoelectrons being proportional to the square of the energy $= R_r = R \left[1 - \frac{\lambda}{\lambda_{K, L, \dots}} \right]^2$, where R is the range of the photoelectrons if the whole of the energy of the incident quantum has been given to it. But $R = V^2/44$ mm. in air, where V is the kinetic energy in kilovolts. Since $V^2 = 152 \cdot 5/\lambda^2$, then $R = 0 \cdot 0042/\lambda^2$ mm.‡ in a substance of density unity, on the assumption that the range is inversely proportional to the density.§ The ranges in other materials were derived assuming again inverse proportionality with the density and using the appropriate values of $\lambda_{K, L}$ and λ . The whole process is evidently approximate and intended to give the order of magnitude of the electron "ranges." As the radiations employed are in general very heterogeneous and the significance of the equivalent wave-length by no means clear, we must guard against a too close identification of the properties of a beam having a certain λ_e and the strictly monochromatic beam of rays with this wave-length, more particularly as we are dealing with the effects to be observed in a region of wave-lengths in which the heavy elements show their characteristic absorption limits.

* *Loc. cit.*

† Mayneord, *loc. cit.*

‡ Mayneord, 'Brit. J. Rad.,' vol. 2, p. 373 (1929).

§ Terrill, 'Phys. Rev.,' vol. 21, p. 476 (1923).

Table V.

Wave-length. Å	Copper.		Tin.		Silver.		Gold.		Platinum.		Lead.	
	Experi- ment.	Theory.	Experi- ment.	Theory.	Experi- ment.	Theory.	Experi- ment.	Theory.	Experi- ment.	Theory.	Experi- ment.	Theory.
0.1	6.0	4.8	18.0	22.5	7.0	19.5	12.5	12.9	13.2	13.6	7.0	6.8
0.2	11.5	16.1	32.0	16.7	13.0	30.0	30.0	35.5	33.0	33.7	24.0	28.6
0.3	10.5	13.1	21	14.7	15.0	10.0	20.0	19.9	17.0	15.7	9.8	8.7
0.4	4.4	9.4	8.7	—	7.5	3.2	6.5	7.9	5.0	5.1	2.6	1.0
0.5	—	5.5	—	27	—	8.5	—	2.0	—	0.95	—	0.05

It will be seen that for the lighter elements, though the maximum observed is predicted, the absolute values of the calculated and observed values do not agree. On the other hand for the heavy elements, Au, Pt and Pb, the agreement is considerably better than would be expected. It appears, therefore, likely that the equations given agree at least qualitatively, with the observations. Some of the difficulties in a complete theoretical investigation have been indicated above.

Experiments with Scattered γ -rays.

Consider a narrow beam of γ -radiation of wave-length λ incident on a small scattering sphere of material of low atomic number such as carbon. Then it is well known that the secondary γ -radiation emitted by the scattering material under the action of the primary rays, will differ in wave-length from the primary radiation by an amount $\delta\lambda$, where* $\delta\lambda = h/mc (1 - \cos \phi)$, ϕ being the angle between the original direction of the radiation and that of the scattered quantum.

For γ -radiations the shifts of wave-length are of great importance. Thus on scattering at 180° to the primary beam an increase of wave-length of 0.048 Å. takes place, implying that γ -rays whose initial wave-length may be of the order of 0.022 Å. will be transformed into radiations of wave-length 0.070 Å. on scattering.

We should therefore expect from the curves previously given, that if we performed experiments on the scattering of γ -rays around a light object, that the precise distribution observed would depend largely on the material of which the ionisation chamber was constructed, since the wave-length is dependent on the direction of scattering and the instrument so sensitive to

* Compton, "X-rays and electrons," p. 266.

change of wave-length. The amounts of radium required to carry out this investigation using a very small ionisation chamber are prohibitive and the following experiment was therefore carried out.

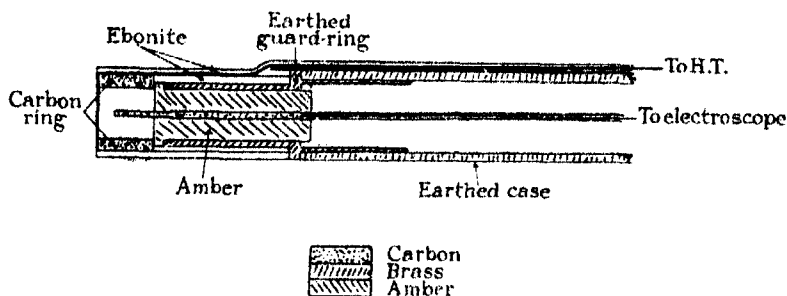


FIG. 4.

A very small ionisation chamber, as shown in fig. 4, was first constructed. The ionisation chamber consists of a carbon ring 2 mm. thick forming part of the outer wall, while a carbon rod 0.6 mm. diameter is used as central electrode. The length of the chamber is 6.0 mm. and the diameter 5.0 mm. The end of the chamber consists of graphited paper. The central rod is connected to a Wilson tilted electroscope by means of a thin wire insulated by means of ebonite bushes from a surrounding earthed brass tube approximately 1 metre long. The wire is covered with ebonite capillary tubing. The high tension wire is led along outside the cable and also completely enclosed in ebonite capillary tubing, only entering the chamber near its end. In this way we prevent the lead from acting as a long ionisation chamber, since the difference of potential between the wire and brass case never exceeds 5-6 volts and the distance between them is 1.0 cm. An earthed brass guard runs almost the whole length of the amber insulation of the central rod in order to prevent as far as possible leakage through the amber under the action of the γ -rays. The remainder of the construction may be seen from fig. 4.

Preliminary experiments showed that saturation was attained in the chamber with approximately 10 volts difference of potential between ring and central electrode, but there are no signs of ionisation by collision below 90 volts. In all experiments a difference of potential of 50 volts was maintained. The electroscope was protected by lead blocks 2 inches thick placed between the radium and instrument. The primary ionisation was observed in the small chamber when 200 mg. Ra (contained in six platinum needles, 35 mm. long, 2 mm. diameter, wall thickness 0.6 mm. Pt) were placed side by side on a card and

held at a distance of 4 cm. from the wall of the chamber, the centre of the group of needles lying on a line perpendicular to the axis of the chamber and passing through its geometrical centre. The increase in intensity was now measured when beeswax 10 cm. thick was brought up below the chamber, the beeswax being grooved so as to enable the ionisation chamber to be buried in the wax up to its centre line. This increase of intensity was measured when the bottom half of the internal surface of ionisation chamber was covered with each of the metal foils in turn. The scattered γ -rays must now pass through the foils on their way to the air of the chamber. The results of the experiments are shown in fig. 5 where the total intensity due to both primary and the scattered rays is plotted against the atomic number of the element concerned. It will be seen that, as was to be expected, in the region of wave-lengths lying at about 0.07 Å. ionisation chambers of different materials are variously sensitive to the radiations. The experiments indicate that in measurements on the distribution of γ -radiations in extended media the ionisation chamber should once more be composed of materials having the same atomic number as the medium in which the measurements are to be made. A special case of interest, namely, the distribution of γ -radiation in animal tissues has been considered by Bruzau recently, and similar conclusions come to, with respect to the measurement of γ -rays scattered in water.

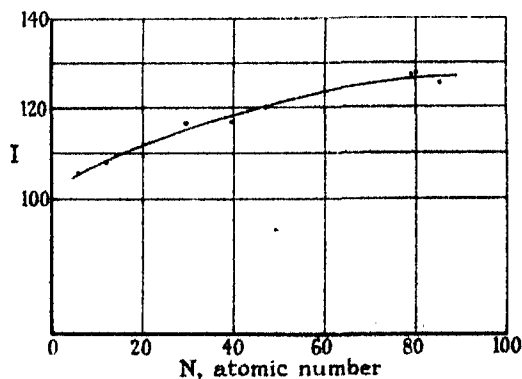


FIG. 5.

Experiments with Animal Tissues.

We wish finally to describe experiments in which an attempt was made to make measurements with an ionisation chamber, one side of which consisted of animal tissues. The physical aspects of the results only will be discussed.

The graphited paper chamber which previously served as standard was here

abandoned as still showing too great variation compared to a standard air chamber to act as the standard of comparison against tissues, since the latter were themselves likely to be approximately "air" substances. We have therefore, constructed a small cylindrical chamber of graphited cellophane, 14.7 mm. long, 12.7 mm. diameter, having walls 0.002 cm. thick. The chamber is sealed with a thin celluloid end, the cylindrical portion being made by wrapping the graphited cellophane around a brass former and sealing with a saturated solution of cellophane in amyl acetate. This chamber was tested against the air chamber as before and it will be seen that from 60 K.V. with 0.5 mm. Al filtration to 130 K.V. and 10.7 mm. Al filter, the deviation is not greater than the experimental error of 2 per cent.

Peak voltage.	Filter.	Ratio.	Peak voltage.	Filter.	Ratio.
KV.	mm. Al		KV.	mm.	
60	0.5	1.67	130	0.5	1.69
80	0.5	1.70		1.0	1.69
100	0.5	1.69		2.0	1.66
120	0.5	1.69		4.0	1.70
130	None	1.62		6.0	1.68
				10.7	1.69

During preliminary experiments it was soon found that the introduction of wet fresh animal tissues into an ionisation chamber quickly ruined the insulation of the gold leaf system but that dried tissues could very easily be used. Moreover, the dried tissues caused very definite divergences between the two ionisation chambers. We will here, however, describe the results of a set of recent experiments in which the difficulties were overcome and experiments made with wet tissues.

The ionisation chamber (fig. 6) consists of a carbon ring A on to which is

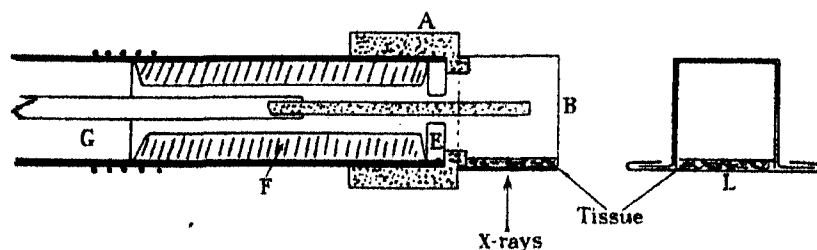


FIG. 6.

fixed a graphited celluloid cube B having one side and base removed. The animal tissue lies on a strip of graphited celluloid L which is itself held in

position by means of a second strip bent round the ionisation chamber and having small flanges turned outward. The central carbon rod of the ionisation chamber passes into the chamber through a hole in a celluloid disc E 2 mm. thick, the hole being sufficiently large to allow the rod to pass without touching the celluloid; 1 mm. clearance is allowed. The rod is insulated by means of amber at G, the insulation being thus far removed from the chamber, while around the outside of the brass cable carrying the amber and carbon ring, a small heating coil ("Pladuram" wire 0.117 mm. diameter) is wound which enables the surface of the insulating material to be kept at a slightly higher temperature than the chamber itself. The brass cable is protected with lead F, 3 mm. thick, so as to avoid stray ionisation in the air, the volume of air being also reduced to a minimum. It was found that in this way the introduction of wet substances into the ionisation chamber caused no appreciable natural leak to develop. A number of preliminary experiments were performed. It was first verified that the heating of the apparatus caused no appreciable variation in ionisation current in the chamber.

In these experiments each ionisation chamber, the standard cellophane and the tissue chamber, had separate insulating cables of different lengths and therefore capacities. These cables were led to a specially constructed mercury throwover switch by means of which either chamber could be connected to the gold leaf electroscope, the switch being carefully electrostatically shielded and situated near the electroscope. The observer could, therefore, without disturbing the arrangement, make readings with cellophane chamber and tissue chamber alternately. This procedure was adopted throughout, the mean of three readings of each chamber being taken, the readings of the two chambers being made alternately. In order to find the effects of the differences of length of cables, as nearly as possible similar cellophane chambers were fitted to each cable. For a number of equivalent wave-lengths the ratio of the ionisation currents observed with the two chambers side by side was obtained. The ratio was independent of the wave-length and equal to 0.77. The tissue chamber now replaced one of the cellophane chambers, the base of the chamber being constructed of graphited cellophane in place of animal tissue. The ratio, corrected for the difference in volume of the tissue chamber when containing the tissue on top of the cellophane, was 0.78. Thus any deviation subsequently observed could not be due to the celluloid or other materials used in the construction of the tissue chamber.

It is clear that we would expect theoretically the animal tissues to be equivalent to a cellophane wall for very short wave radiations, say for γ -rays. The mean

of the ratios of the ionisation currents observed in the cellophane and tissue chambers for γ -rays was 0.78, all types of animal tissue agreeing with this value within the limits of experimental error.

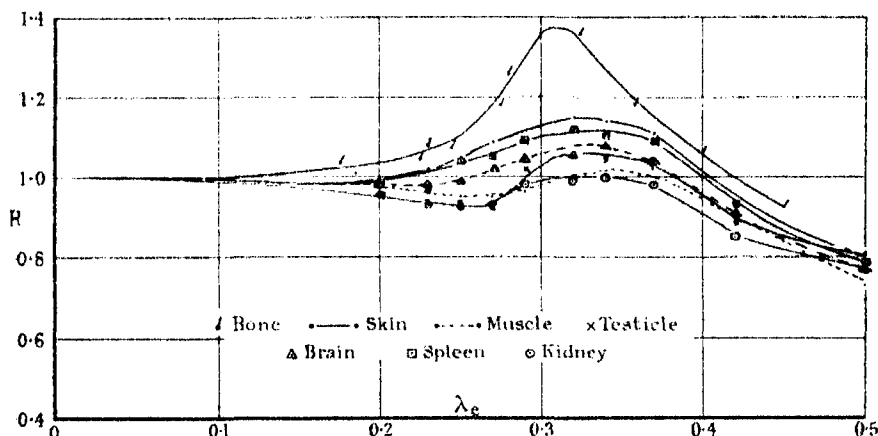


FIG. 7.

All experimental results given below have been corrected so as to give the value 1.00 throughout for an air-like substance, for instance, graphited cellophane.

A healthy rat was killed and immediately dissected, blocks of skin, testicle, brain, spleen, kidney, muscle, heart and liver being taken for examination. Each block of tissue was frozen on to the stage of a carbon dioxide freezing microtome and a section exactly 1 mm. thick was cut. This section was then trimmed to the correct size to cover the floor of the ionisation chamber, transferred to the celluloid strip and the ionisation currents in the chamber observed simultaneously with the current in the cellophane chamber as described above. The results of one set of experiments are given in fig. 7. The curve for bone was obtained by laying slips of human compact bone, approximately 1 mm. thick, in the position normally occupied by the single slice of tissue.

It will be seen that for short equivalent wave-lengths that the currents in the two chambers do not diverge very greatly from each other, but that for the longer wave-lengths the tissues diverge from strict air equivalence and from each other. The rise in the ratio is presumably to be interpreted as the rise to importance of the fluorescent absorption in the small amounts of heavy elements in animal tissues, but in view of the difficulty of estimating the relative importance of the wall radiation and the ionisation in the air itself we cannot at the moment carry the theoretical consideration further. The

subsequent fall in the ratio, is, as in the case of the foils, to be interpreted as the results of absorption in the walls of the chamber and decreasing penetration of secondary electrons. It appears, however, that for long wave radiations ($\lambda_e = 0.3 \text{ \AA}$) a standard air wall ionisation chamber would underestimate the energy absorption in an animal tissue, but appears to be quite suitable for very short wave-length radiations. Further experiments in order to obtain more quantitative information are proceeding.

Summary.

The paper describes experiments on small ionisation chambers artificially made sensitive to different X- and γ -radiations by the insertion of foils of different elements. It is shown that compared to an air chamber these ionisation chambers show a maximum sensitivity in the region of medium wave-lengths. The theory of the occurrence of this maximum is discussed.

A small ionisation chamber suitable for γ -ray measurements is described, and it is shown that the relative intensity of primary and secondary scattered beams of rays was differently estimated according to the materials of which the chamber was constructed.

The experiments were extended to include the effects to be observed with ionisation chambers containing animal tissues. It is shown that again a region of maximum sensitivity is observed and that various tissues diverge by varying extents from "air equivalence." The significance of these observations is briefly discussed.

The Swelling of Charcoal. Part I.—Preliminary Experiments with Water Vapour, Carbon Dioxide, Ammonia, and Sulphur Dioxide.

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(Communicated by D. L. Chapman, F.R.S.—Received April 16, 1930.)

The experiments of Meehan* having shown that charcoal increases in volume when taking up carbon dioxide, it became an obvious step to correlate this expansion with the quantity of gas adsorbed.† In this paper a form of extensometer is described which, while sufficiently sensitive and accurate for the measurement of the percentage linear expansion (x) of a rod of wood charcoal, was yet compact enough to permit its being sealed up in an all-glass apparatus, so that simultaneous determinations could be made of the weight (s) of gas taken up per unit weight of the adsorbent.

The graphs obtained by plotting the variables x and s have certain interesting characteristics which it will be convenient to describe before dealing with the detailed results. As fig. 1 shows, the coefficient dx/ds increases steadily with s ; thus far the charcoal behaves similarly to many of the common gels, which contract proportionately less in the later stages of drying, owing to the micellæ coming in contact with each other. The swelling of charcoal, however, appears to follow a more regular course than that of the elastic gels, and in the case of ammonia, carbon dioxide, and sulphur dioxide is given within the limits of accuracy of our experiments by hyperbolic equations of the type

$$x = k \frac{s}{S - s} \dots$$

where k and S are constants characteristic of each gas. In fig. 1 the experimental values of x have been plotted (for convenience of representation) against s/S . The smooth curves for ammonia, carbon dioxide, and sulphur dioxide are the graphs derived from equations of the above form, using appropriate values of the constants. An additional term (a small additive constant over the experimental range) is necessary to represent the behaviour of water vapour.

* Meehan, 'Proc. Roy. Soc.,' A, vol. 115, p. 199 (1927).

† Bangham and Fakhoury, 'Nature,' vol. 122, p. 681 (1928). The relation between the expansion and the sorption there given was not confirmed when the experiments were extended to cover a wider range of values.

The values of the constants k and S for the four gases are set out in the following table; they refer in all cases to experiments carried out at room

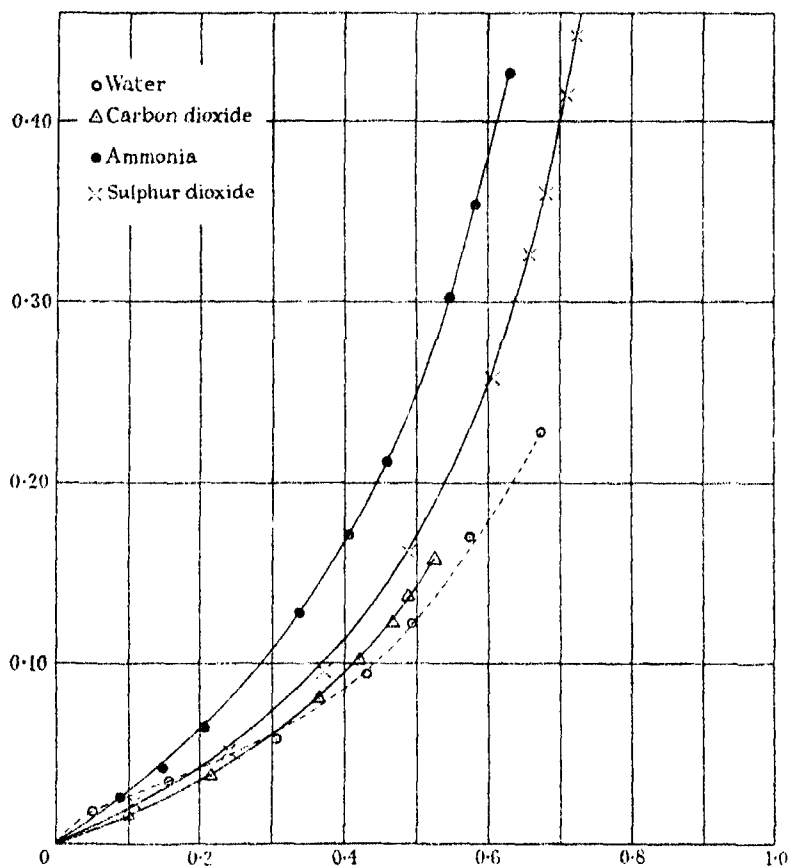


FIG. 1.—Expansion of Charcoal at Room Temperature. Abscissæ, Fractions of Limiting Sorption Values, Ordinates, Linear Expansion per cent.

temperature. It is noticeable that the S -values (which are calculable from the observations to within a few per cent.) show approximate agreement with the regularity observed by Gurvitch* in the case of the saturation sorption values, that is to say they represent nearly equal volumes of the normal liquid at the experimental temperature. The product SV , (where V_s is the specific volume of the liquid adsorbate) is, however, rather smaller in the case of the denser liquids.

* Gurvitch, 'J. Russ. Chem. Soc.,' vol. 47, p. 805 (1915).

Table I.
(Temperature 18° to 20° C.)

	H ₂ O.	CO ₂ .	NH ₃ .	SO ₂ .
<i>k</i> (per cent.)	0·110	0·143	0·252	0·1705
<i>S</i> (grams per gram of charcoal)	0·158	0·139	0·112	0·210
<i>SV</i> _g (cubic centimetres)	0·158	0·177	0·183	0·151

Experimental.

The extensometer used was a nickel instrument constructed to the authors' design by Messrs. Becker & Co. It operated on much the same principle as that employed by Meehan, but a scale and pointer were substituted for the optical lever. The charcoal rod was placed between the adjustable jaws A, A' (see fig. 2). On expanding, it raised the distance-piece and knife-edge fixed to the upper jaw, causing a rotation of the lever B about a pair of coplanar knife-edges at C. Vibration of the pointer was prevented by two light return-springs at D, while the body of the extensometer itself was held firmly inside the containing tube by the compression-springs E, E', E''.

The lever magnified the movement about 40 times, so that with the aid of a reading microscope an expansion of one two-thousandth of a millimetre could be detected with certainty. The interposition of the curved surface of the containing tube between the pointer and measuring instrument rendered necessary the application of an optical correction to each reading.

Perhaps because the return-springs were rather too light, the extensometer could not always be relied upon when a change occurred in the direction of movement (as, for example, when heating and cooling *in vacuo*). In consequence, the zero-point reading in each experiment was subject to a greater error than readings taken when the pointer was moving continuously in the direction of expansion.

This error could be estimated by carrying out series of experiments under precisely reproducible conditions; it never exceeds 4×10^{-3} mm.

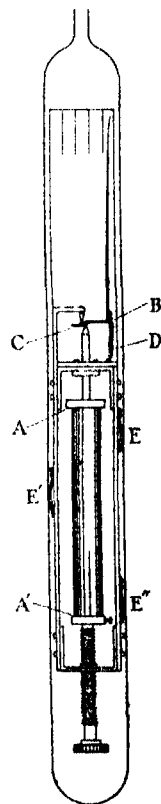


FIG. 2.

The large deadspace of the extensometer vessel, a great portion of which was subject to the fluctuations of room temperature, rendered the adsorption values far more difficult to determine with accuracy. On account of the necessity for introducing successive and carefully controlled quantities of gas to the charcoal a method was adopted whereby the gas was generated, as required, from solid materials contained in a detachable weighing tube. This tube, or generator, which carried a tap, and in some cases also a phosphorus pentoxide tube, connected through a push-join with a capillary-tube system, from which other taps led on the one side to the sorption vessel and on the other to the drying train and pumps. Between each successive generation of gas the taps carried by the weighing tube and by the extensometer vessel were closed; dry air was admitted into the connecting capillary and the weighing tube detached and weighed. The unadsorbed residues of gas in the extensometer vessel and capillary system were estimated by means of a mercury manometer sealed to the former. The deadspaces were calibrated with hydrogen, an appropriate correction being applied for the sorption of this gas by the charcoal. An error in estimating this correction would affect the *s*-values very slightly in the case of carbon dioxide and quite inappreciably those of the other gases.

Between successive experiments the extensometer vessel was submitted to prolonged vacuum-heating at 220° C. in an electrically controlled furnace. The evacuating system comprised a condensation pump backed by a rotatory oil pump. Unquestionably the treatment did not suffice to remove the last traces of some of the gases, but the presence of the extensometer and the large volume of the containing tube rendered it both dangerous and difficult to submit the charcoal to more drastic treatment. The method of correcting the results for the presence of these small residues is described in the next section.

The Charcoal.—A piece of pre-war German willow charcoal was used, cut into the form of a rod $8 \times 0.8 \times 0.8$ cm. No means being available for its high-temperature treatment, no attempt was made to reduce its ash-content by treatment with acid. The ash-content was comparatively low, however, being no more than 0.9 per cent. The "block" density of the specimen was 0.30 grams per cubic centimetre.

The experimental gases were generated as follows:—

Ammonia.—The gas, after preparation and liquefaction, was fractionally distilled over solid potash and passed through phosphorus pentoxide into a tube containing carefully dried silver chloride. From the latter

it was driven, as required, into the weighing tube, which also contained silver chloride. The gas so treated was sufficiently dry to pass through a good phosphorus pentoxide tube without the latter becoming visibly affected.

Water Vapour.—From hydrated copper sulphate contained in the weighing tube.

Carbon Dioxide.—From sodium bicarbonate and phosphorus pentoxide ; a phosphorus pentoxide tube was sealed to the weighed generator to prevent loss of water.

Sulphur Dioxide.—From normal sodium sulphite and phosphorus pentoxide ; here also a phosphorus pentoxide drying tube was used.

Summary of Results at Room Temperature.

The reproducibility of the results with ammonia and sulphur dioxide was slightly interfered with by the presence of the small residues of these gases which resisted removal by the normal heat treatment. An extended series of experiments carried out with ammonia, however, clearly showed that the effect of these residues was slightly to displace the x, s curves parallel to themselves ; the necessary zero-point corrections could, therefore, be estimated by superposing the graphs on those given by the uncontaminated charcoal.

The measurements with water vapour at low s -values showed a curious inconsistency which could not be ascribed to the same cause, since the irregularity disappeared when higher values were reached. The results of several sorption experiments with this substance are illustrated in fig. 3 by plotting x against $s/S - s$. According to the hyperbolic equation, the result should be a linear graph passing through the origin ; since the prolongation of the line cuts the axis well above this point, water vapour must be regarded as exceptional, in that even the first traces cause a marked expansion. Further investigation of this interesting region was unfortunately impossible, owing to the very considerable errors involved in estimating small sorption values. Apart from this irregularity the s, x relations appear no different from those of the other gases, in spite of the near approach to saturation conditions, and the generally anomalous behaviour of water as an adsorbate.

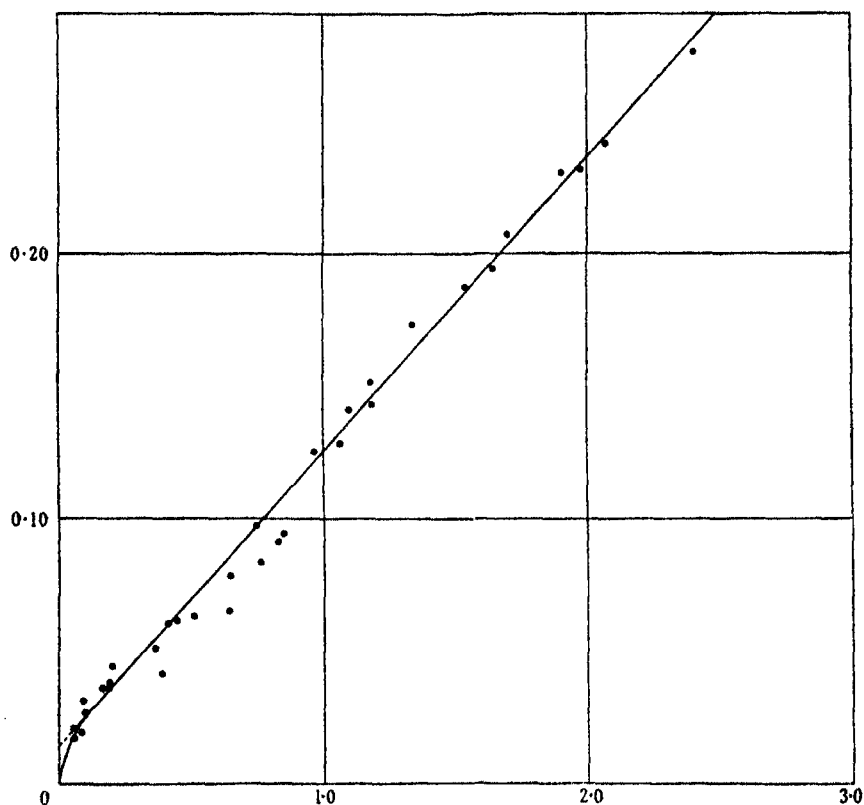


FIG. 3.—Water Vapour at 20°. Abscissæ $s/(S - s)$. Ordinates, x per cent.

The following table summarises the results of typical experiments with the four gases, and gives, for comparison, the x -values calculated from the hyperbolic equations.

Table II.

 s = sorption value in grams per gram of charcoal. x = linear expansion per cent. at room temperature (18° to 20° C.).

WATER.					CARBON DIOXIDE.			
$S = 0.158$ gram. $k = 0.110$ per cent.					$S = 0.139$ gram. $k = 0.143$ per cent.			
$s.$	$s/S.$	x obs.	x calc.	Diff. $\times 10^3.$	$s.$	$s/S.$	x obs.	x calc.
0.0081	0.051	0.018	0.004	14	0.0136	0.098	0.016	0.015
0.0251	0.158	0.035	0.021	14	0.0294	0.213	0.038	0.038
0.0484	0.306	0.058	0.048	10	0.0506	0.364	0.081	0.081
0.0680	0.430	0.094	0.082	12	0.0582	0.419	0.102	0.103
0.0778	0.492	0.122	0.106	16	0.0647	0.465	0.123	0.124
0.0906	0.573	0.170	0.148	22	0.0676	0.486	0.137	0.135
0.1066	0.674	0.238	0.228	10	0.0729	0.524	0.158	0.157

AMMONIA.				SULPHUR DIOXIDE.			
$S = 0.112$ gram. $k = 0.252$ per cent.				$S = 0.210$ gram. $k = 0.1705$ per cent.			
$s.$	$s/S.$	x obs.	x calc.	$s.$	$s/S.$	x obs.	x calc.
0.0099	0.089	0.026	0.025	0.0221	0.105	0.023	0.020
0.0165	0.148	0.042	0.044	0.0501	0.239	0.052	0.053
0.0227	0.202	0.064	0.064	0.0777	0.371	0.096	0.101
0.0378	0.337	0.128	0.128	0.1021	0.486	0.162	0.162
0.0455	0.406	0.171	0.172	0.1377	0.656	0.329	0.327
0.0512	0.458	0.212	0.212	0.1424	0.679	0.361	0.361
0.0611	0.546	0.303	0.303	0.1486	0.708	0.414	0.414
0.0653	0.583	0.354	0.353	0.1522	0.724	0.448	0.447
0.0706	0.631	0.427	0.428	0.1532	0.730	0.461	0.461

Discussion.

Considered in conjunction with the essentially anisotropic macro-structure of charcoal, the observation of Meehan that the expansion accompanying adsorption is equal in all directions provides sufficient evidence that adsorption is a process affecting the fine internal structure of the walls of the macropores, and not one concerned merely with their free surfaces. The effect of the macropores is thus to magnify the observed expansion of a given weight of charcoal in proportion to the "block" volume.

Of recent years much evidence has accumulated which suggests that molecules adsorbed on solids have, in many cases, freedom of movement in directions

parallel to the surface.* Where the surface is plane or convex, this could hardly give rise to any distending effect, but it might well be that in the case of such a fine-structured solid as charcoal the adsorbed film exerts a wedge-like action resulting from molecular bombardment taking place at sharp re-entrant angles in the surface.

With the rise of concentration at the free surface of the charcoal there would be a more than proportionate increase in the surface pressure, as the "incompressible" volume associated with the molecules approaches more and more closely the total space available for the adsorbed phase.†

The limiting sorption values S are to be distinguished from the saturation values found by direct measurement of the adsorption in contact with saturated vapours. Further experiments with water vapour have indicated that the condition of saturation is reached without serious departure from the hyperbolic relationship. That the S -values of the four substances examined represent nearly equal volumes of the normal liquids appears to signify that the total space available for the adsorbed phase (which, as saturation is approached, must approximate more closely to the normal liquid condition) is nearly equal in all four cases. It does not, however, follow that the films are all of equal thickness, for possibly their area is considerably greater in the case of substances which have smaller molecules.

The Effect of Temperature : Experiments with Ammonia.

Since the experimental temperature, though nearly constant in any one experiment, varied somewhat from one run to another, it was of some importance to determine the influence of this factor on the expansion measurements. Four experiments were carried out with ammonia, covering the range from 0° to 75° C. It was found that for any given value of s the corresponding x was slightly greater at higher temperatures. So small was the variation, however,

* See, for example, Volmer and Adhikari, 'Z. Physik,' vol. 35, p. 170 (1925); Volmer, 'Z. Physikal Chem.,' vol. 115, p. 255 (1925); Frenkel, *ibid.*, vol. 33, p. 366 (1925); 'Chem. Soc. Annual Reports,' vol. 25, p. 350 (1928), where further references are given.

† Schofield and Rideal, 'Proc. Roy. Soc.,' A, vol. 109, p. 57 (1925), propose, as the equation of state of molecules adsorbed at the surfaces of solutions, an equation

$$F \left(\frac{1}{\Gamma} - B \right) = i R T,$$

where F is the surface pressure, Γ the (excess) surface concentration, B a constant standing for the smallest area the (gram) molecule can occupy, and i a constant depending on the lateral cohesion between molecules. The similarity of form between this and the empirical equation for the expansion is probably not without significance.

that these experiments yielded no indication as to whether the temperature changes had influence on one or on both of the constants k and S . If S be supposed constant (an assumption which finds some support from considerations dealt with in the last section), k is found to vary roughly in proportion to the absolute temperature, taking the following values at the temperatures stated :—

T (° absolute)	273	293	321	348
k (per cent.)	0·231	0·252	0·266	0·306

It should be remarked, however, that no high degree of accuracy is claimed for these measurements, which aimed primarily at assessing the errors introduced into the experiments previously described by the fluctuations of room temperature.

We are indebted to Dr. Stradling and Dr. Meehan for details of the extensometers used by them at the Building Research Laboratories, and also for adding to our stock of charcoal suitable for extensometric experiments.

Summary.

An apparatus is described by which the linear expansion of a charcoal rod can be measured simultaneously with the quantity of adsorbed gas causing it. The expansion (x) is found to be related to the adsorption value (s) by equations of the type

$$x = k \frac{s}{S - s}$$

where k and S are constants. The values of the latter constant for the four gases examined represent nearly equal volumes of the normal liquids at the experimental temperature. The hypothesis is advanced that the expansion results from the pressure exerted by the adsorbed molecules at sharp re-entrant angles in the surface of the adsorbent. The expansion caused by the adsorption of a given quantity of gas increases with the temperature.

The Distribution of Velocity in an Open Channel of Rectangular Section.

By T. B. ABELL, M.Eng., and J. H. LAMBLE, B.Eng.

(Communicated by J. Proudman, F.R.S.—Received August 5, 1930.)

The particulars given in this short note have been obtained during the calibration of a hydraulic channel recently completed at the University of Liverpool. The immediate object of the calibration was to explore the central portion of the stream and to obtain the limits of the area of cross-section over which the velocity of flow parallel to the channel might be regarded as sensibly uniform. Measurements of velocity were made at a range of levels and also at a series of verticals in the same transverse plane. As the work proceeded, from the nature of the observations, it seemed worth while taking the opportunity of mapping completely the contours of constant axial velocity and so to supplement the somewhat limited experimental data* previously obtained under laboratory conditions for the flow in a uniform channel.

The Apparatus.—Water was circulated in a closed circuit by a speed-regulated shunt-wound motor driving an axial flow pump which drew water from the downstream end of an open steel channel of rectangular cross-section, and delivered it through a pipe to the upstream end of the channel. The arrangement of the channel is illustrated by the plan, elevation and sections in fig. 1. Its length between the end plates is 66 feet; everywhere its transverse section is a rectangle. It is of the uniform width of 5 feet for 44 feet at the downstream end. At the inlet end the channel is bulbous in plan, attaining a maximum width of 7 feet, contracting by gentle curves of 41 feet radius into the uniform channel. Water is delivered vertically upwards into the bulbous end through a pipe subdivided by axial baffles *L* in two vertical planes, transverse and longitudinal, in order to destroy as far as practicable the "spin" of the water as it comes round the bend to enter the channel. The longitudinal division was adjusted so as to secure equal volumes of flow in each half of the channel. It will be noted later that the calibration showed that, with the setting of the longitudinal baffle, the flow was not equally

* Gibson, 'Proc. Roy. Soc.,' A, vol. 82, p. 149, 1909

United States Geol. Survey, Water Supply & Irrigation Papers, No. 95, Calibration of Cornell Channel.

'Hydraulique,' M. Flamant. Bazin. D'Arcy.

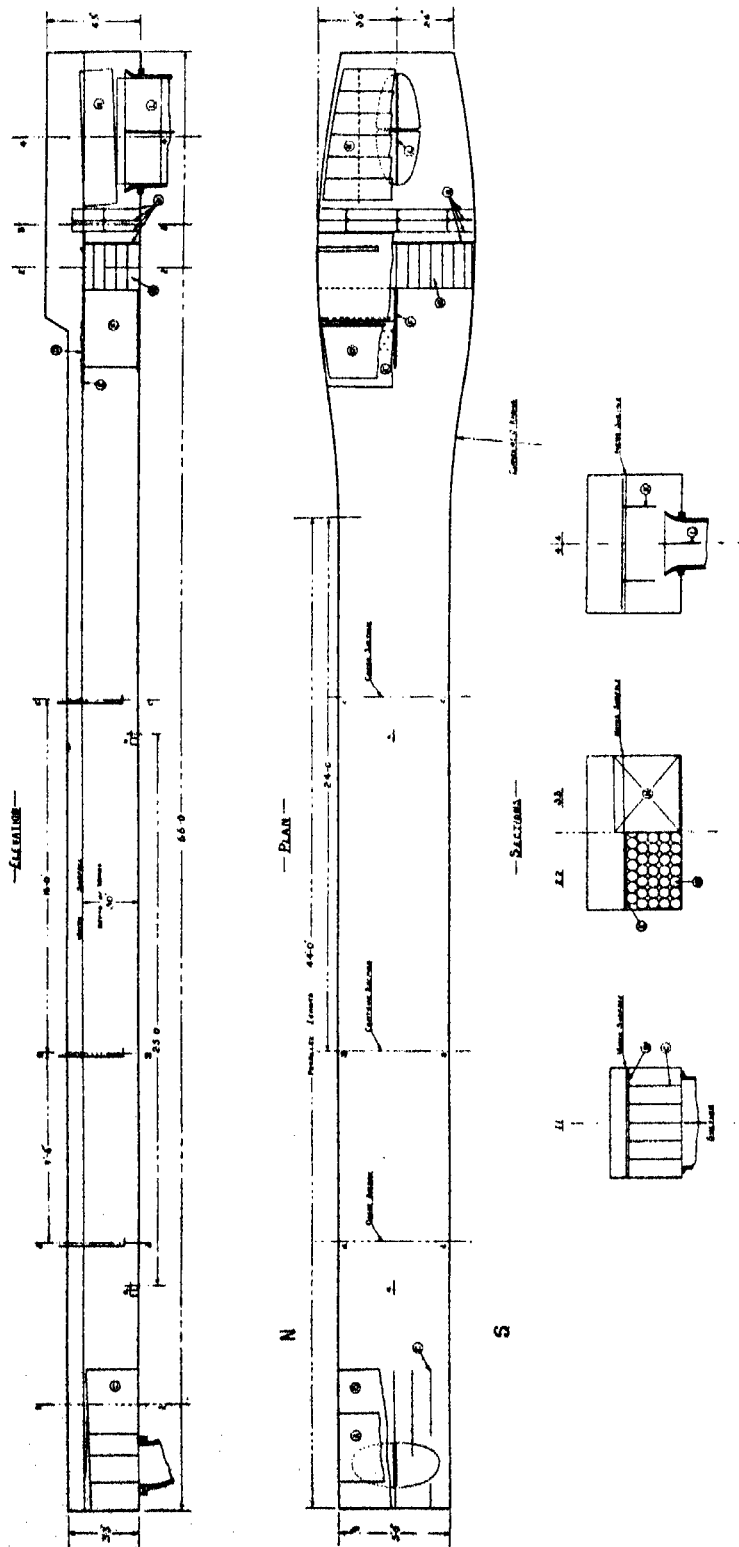


FIG. 1.

distributed, that on one side being the greater by 1 per cent. In order to obtain as uniform a velocity of total flow as possible throughout the length of parallel portion of the channel, resistances were placed across the widest portion of the channel. These consisted of four vertical zinc plates H, perforated with holes $\frac{1}{2}$ inch in diameter. These destroyed the larger eddies in the stream escaping from the pipe. The flow was then given an axial direction by a nest of copper pipes G, 6 inches in diameter and 2 feet long, placed at the maximum width of the channel. In order to quell wave disturbances a wood baffle K, with two deep keels placed longitudinally, floated immediately over the inlet pipe; in addition, a thin steel plate E extended horizontally across the tank over the top of the copper pipes, just below the normal water level in the main channel. On its upper face were fitted three breakwaters to trap any surface disturbances. On the downstream side of the pipes this horizontal plate was perforated with 1 inch holes, so that water from below it could feed the space above the top of the plate and thus avoid any marked discontinuity where the plate terminated. As the water flowed through the perforations short waves were formed which would have persisted along the surface. These were quelled by floating over the perforations a sheet of cartridge paper D. This gave a smooth surface to the stream. At the central plane of the channel this plate was supported by a vertical thin steel plate F, resting on a wood base 2 inches wide and 1 inch deep, and by pillars, one on each side, $\frac{1}{8}$ inch in diameter. Except for these plate supports the flow was entirely unrestricted on the down stream side of the copper pipes, through which the flow was mainly parallel to the axis of the channel.

At the exit of the channel a series of vertical plate baffles C, parallel to the sides of the channel, were provided below a horizontal plate baffle B, which was about three-quarters of an inch below the surface of the stream. The energy of that portion of the stream above the plate was absorbed by a short beach A, formed by sloping the upper baffle plate. This slope could be adjusted to ensure that no waves were reflected upstream. The arrangement of baffles was quite effective in preventing the formation of large vortices and the drawing of air into the pump suction pipe. At starting there were slight pulsations in the flow with wave disturbances, but after a time the pump settled down to a steady speed with steady delivery. The channel was coated with a bituminous enamel, which initially had a varnish-like surface but became slightly slimy, covering a roughish surface due to a deposit from the water.

Method of Measurement of Velocity.—Two static pressure tubes were fixed at *a, a*, in fig. 1 communicating with large gauge tubes, $1\frac{1}{4}$ inches in diameter,

fitted with micrometer point water-level gauges. These measured the fall of water level from still water to the stream level and also the hydraulic gradient over a length of 25 feet. Velocity was measured by a Pitot tube of the static and total head type. The total head tube was $\frac{1}{8}$ inch in diameter, the static tube had an outside diameter of $\frac{3}{8}$ inch. The datum for positions at which observations of velocity were taken with the Pitot tube was still water level determined by a point gauge.

The two tubes were connected each with a glass gauge tube, internal diameter $1\frac{1}{8}$ inches, placed at the still water level and so under atmospheric pressure. The changes in water level were measured by point gauges operated from above the water surface by a standard screw of 1 mm. pitch fitted with a micrometer head. Successive observations were made with the meniscus always of the same sign. The Pitot tube was entirely freed from lateral vibration. At some positions lateral vibration occurred depending upon the unsupported length of the tube, but this was quelled by providing an intermediate support to the tube.

When the Pitot tube was situated near the surface the readings of the gauges became unreliable guides to the velocity, and in order to obtain the terminal velocities at the surface pieces of confetti paper were timed by electric chronograph, contacts being made by an observer, over a distance of 10 feet situated symmetrically about the plane of observation with the Pitot tube. These provided reliable terminations of the curves of velocity plotted to base of height above bottom of the channel.

Observations.—A rather complete set of observations, amounting to some 1,200, were made over the transverse section S, S, fig. 1. These were plotted in the form of velocity head as ordinates to bases of transverse and vertical position; a surface of velocity head thus obtained facilitated the drawing of curves of velocity head at various depths and at various lateral verticals with the least departure from the actual observations. The curves of velocity head were then converted to velocity. The curves of velocity are shown in fig. 2 for various constant depths and in fig. 3 for varying depths at three different vertical planes, viz.:—at the axial plane and at two planes, 15 inches north and south of the axial plane. Fig. 4 shows contours of uniform velocity. The full horizontal line of fig. 4 is the still water level. The limited attempts made to obtain the form of the free surface were not successful to a degree which would enable it to be definitely stated whether a transverse section of the surface was concave or convex. The contours of uniform velocity are therefore terminated at the dotted horizontal line which is placed at the mean surface level as determined from the static gauges.

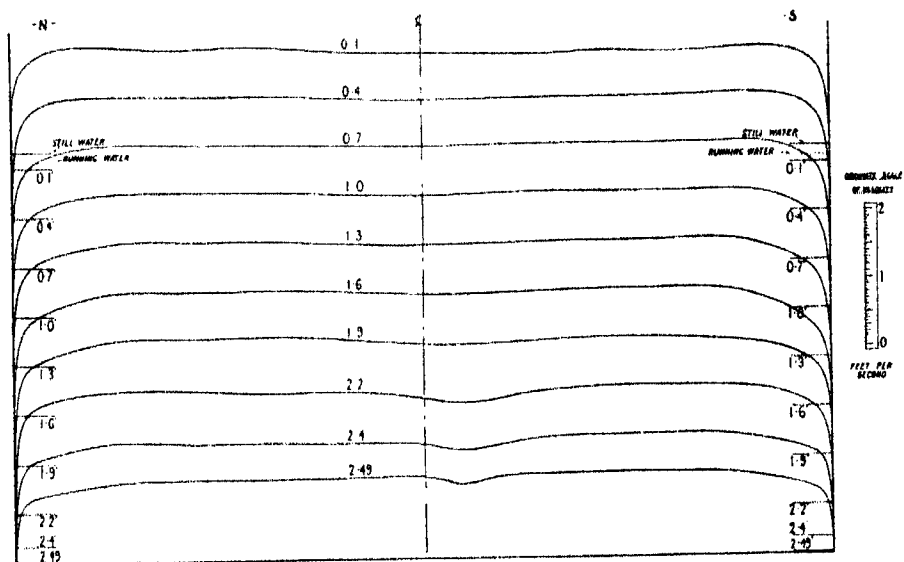


FIG. 2.

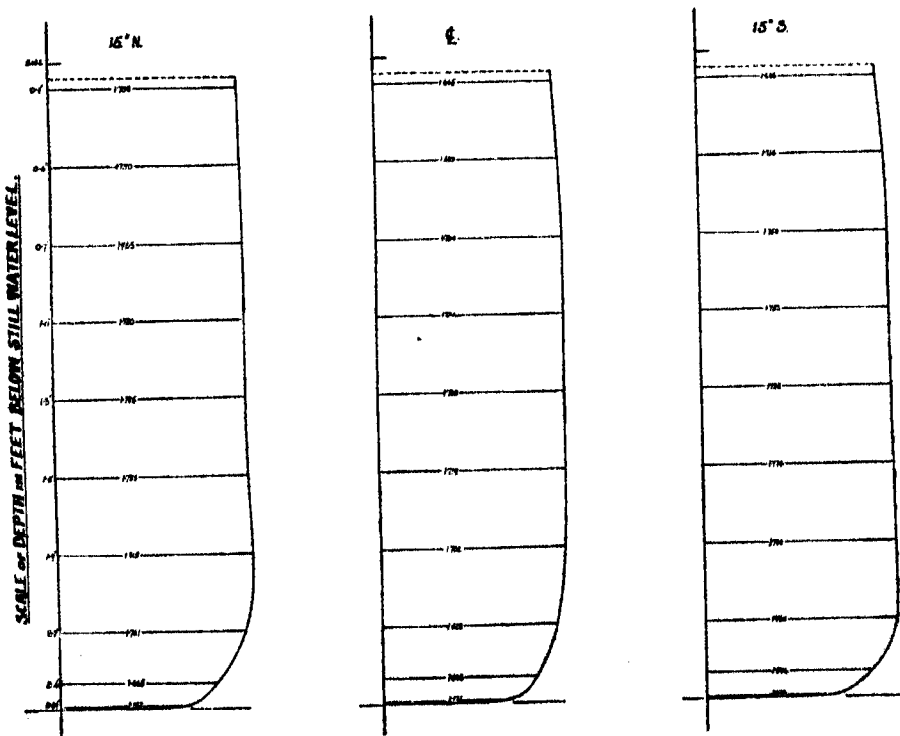


FIG. 3.

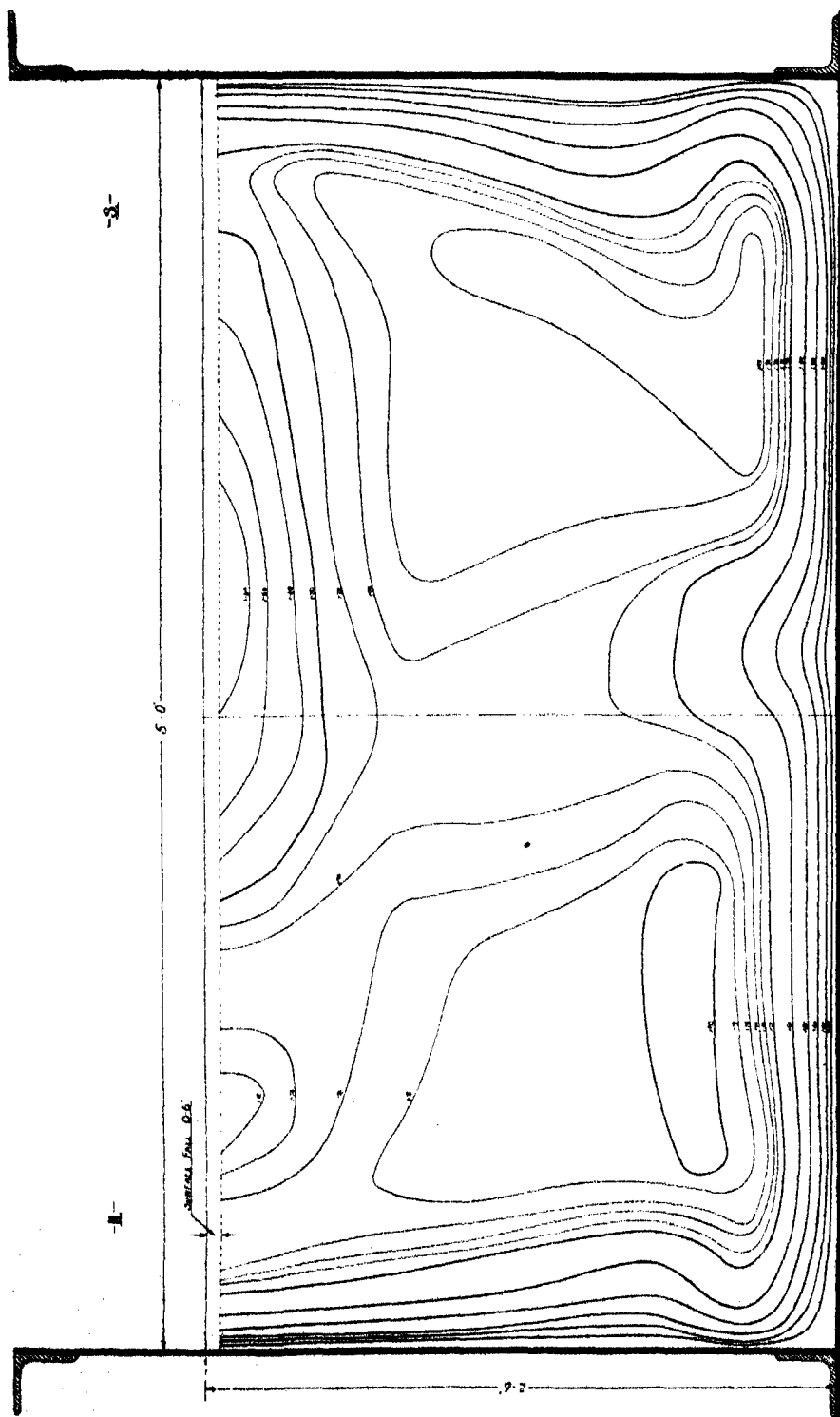


FIG. 4.

Fig. 4 reveals :—

- (a) a lack of symmetry of flow. The discharge indicated by the left half of the diagram is 1 per cent. greater than that of the right half. (The vertical longitudinal diaphragm of the inlet pipe did not extend sufficiently into the pipe to make the discharge on each side of it equal.)
- (b) that velocity increases with depth below the free surface rather rapidly at first, then becoming almost uniform over a wide range, decreasing again as the bottom of the channel is approached :
- (c) that the velocity commences to decrease with depth at a greater distance from the bottom and at a less rapid rate at the central plane than at positions on either side of the central plane :
- (d) that two areas of maximum velocity occur, one on each side of the central plane and rather near the bottom of the channel :
- (e) that over a large area at about half the depth of the channel the velocity was very nearly, though not quite, uniform.

(c) and (d) seemed to need further examination and additional observations were made at transverse sections at *c, c*, and *d, d*. These showed the same general characteristics, indicating that the general distribution of velocity illustrated in fig. 4 persisted and that, throughout the channel, there was a very definite and somewhat marked slowing up of the streams near the bottom at the central plane. It may be that this is created by the central plate on the downstream side of the nest of copper guide tubes, but it is difficult to believe that the effect of the frictional drag of the plate would persist in this marked way throughout the length of the channel.

Endeavours were made to measure the pressure gradient at various levels near the bottom of the channel, but the changes were so small that it could not be established that there was a fall of pressure from the central plane towards the sides. Some observations were made on the motion of surface particles of the stream by noting the lateral movement of pieces of confetti, but as these gave no guide to motion below the surface, observations were made using various liquids. Condensed milk seemed to yield the most useful data when used in the concentrated form. When diluted, it dispersed too rapidly to yield more than general indications that the flow was mainly in the direction of the axis of the channel. When used in the concentrated form, the milk was forced through a pipette under a uniform air pressure, so that drops were discharged

at uniform intervals of time. By regulating the height of the pipette above the water level the drops could be arranged so that :—

- (i) they fell through the water surface,
- (ii) they would be dragged from the orifice by the stream just as they were about to fall.

In the former condition a globule fell through the surface, leaving some of the drop upon the surface.

The globule rapidly passed ahead of the surface portion as it fell through the water, until it reached the retarded portion of the stream, near the bottom of the channel. It was thus possible to observe two particles starting simultaneously from the same point, and by standing over the channel it seemed that the two particles remained practically in the same vertical longitudinal plane, over a length of travel of 22 feet in the parallel portion of the stream. There was no marked evidence of a spiral motion of the fluid.

Drops dragged from the end of the pipette remained on the surface. These were discharged from three positions, the central position and points 15 inches on either side. About 40 observations were taken at intervals of 20 seconds at each position. Particles launched at the centre drifted definitely towards the region of minimum surface velocity, *i.e.*, a little towards the south side of the channel (see fig. 4). From the northern side station there was on the whole a drift towards the north side of the channel, some particles drifting south but most going to the north. From the southern side station nearly all the particles drifted to the south side of the channel, by an average of $2\frac{1}{2}$ inches in the run of 22 feet.

It is clear that the observations here recorded are not definitely appropriate to the condition of established steady flow in a long open channel of uniform rectangular section, firstly on account of the small inequality of discharge in the two halves of the channel, and secondly on account of the proximity of the transverse section at which the observations were made to the inlet baffles. At the same time the distribution of flow revealed, which persists throughout the parallel portion of the channel, is suggestive and perhaps to some degree confirmatory, of the double circulation with axes on each side of the central plane which has previously been suggested.*

The slowing-up of the streams at the centre at the bottom suggests a cause for the formation of mid-river banks observed in some river beds.

* See Gibson. *Loc. cit.*, p. 152.

*Some Phenomena connected with the Transfer of Heat by
Radiation and Turbulence in the Lower Atmosphere.*

By D. BRUNT, M.A., B.Sc.

(Communicated by G. C. Simpson, F.R.S.—Received August 13, 1930.)

1. *The Lapse-rate near the Ground.*

One of the most outstanding facts of observation of the distribution of temperature in the atmosphere is the constancy of the mean lapse-rate of temperature at all heights within the troposphere and in all latitudes. The variation about the mean value, which is roughly one-half of the dry adiabatic lapse-rate, is very slight at all heights greater than a few hundred metres above the ground, but in the layer nearest the ground the extent of the variation is very considerable. At night, and particularly during clear nights in winter, the sign of the lapse-rate in the lowest layer is changed, and the temperature increases with height instead of decreasing. On sunny summer afternoons the lapse-rate in the lowest layers attains very high values, the change of temperature from $\frac{1}{2}$ metre to 1 metre above the ground amounting to the equivalent of 100 to 200 times the dry adiabatic lapse-rate. Observations in the layers still nearer to the ground are not yet available, but the nature of the values hitherto observed suggests that the lapse-rate increases in a marked manner as we approach the surface. This raises a very natural question. Is there any limit to the lapse-rate which is physically capable of formation in the atmosphere immediately above the ground?

In an earlier paper,* I have shown that the outward flux of heat (W-radiation) by radiation can be represented by $-k \frac{\partial T}{\partial z}$ calories/cm.²/min., where k is $115/p_w$ at a temperature of 275° A., p_w being the vapour pressure in millibars, and T representing the absolute temperature at a height z above the ground. The average amount of incoming radiation which has to be disposed of is given (*loc. cit.*) as 0.275 calories/cm.²/min. This, however, is the average over all latitudes, and over day and night, and is too low a value for our present purposes. We shall adopt instead an amount equal to black body radiation at 280° A. amounting to 0.509 calories/cm.²/min. Of this, an amount 0.290

* 'Proc. Roy. Soc.,' A, vol. 124, p. 201 (1929). The name "W-radiation" was introduced in that paper to denote radiation restricted to those wave-lengths within which water-vapour amounting to 0.3 mm. of precipitable water radiates like a black body.

calories/cm.²/min. leaves the ground as W-radiation. These figures would roughly correspond with afternoon sunshine in the British Isles. If we assume the temperature gradient in the layer near the ground to be $\partial T/\partial z$, then it has been shown (*loc. cit.*) that in this layer the amount of W-radiation transported outward by radiative diffusion is $-\frac{1}{2}k \frac{\partial T}{\partial z}$. If the lapse-rate has the value given by the equation

$$-\frac{1}{2}k \frac{\partial T}{\partial z} = 0.29,$$

then conditions will remain steady, since the incoming and outgoing radiations will balance. If the lapse-rate momentarily exceeds this value, it will carry out more radiation than the amount appropriate to steady conditions, and will cool the lowest layers, thus reducing the lapse-rate to the critical value. There is therefore a maximum value of the lapse-rate near the ground, whose value is approximately

$$0.29 \times 2p_w/115 = 0.005p_w$$

or $50 p_w$ times the dry adiabatic lapse-rate (10^{-4} degrees per centimetre). If p_w is 10 millibars, the maximum lapse-rate is about 500 times the dry adiabatic value. With a high sun and a clear sky, the amount of incoming radiation may attain more than double the value we have used as a working figure, and the maximum lapse-rate deduced from the formula may then be more than 1000 times the dry adiabatic. This would correspond to a difference of 1°C . per centimetre.

The argument used in the last paragraph only shows that there is a definite upper limit to the lapse-rate which is thermally possible near the ground. It is not of necessity true that the conditions corresponding to this maximum value are dynamically possible. The argument used above neglects all effects due to turbulence, and does not take into account the stability or instability of the layer in question.

2. The Combined Effects of Radiation and Turbulence.

It was shown in the earlier paper referred to that in the atmosphere the vertical transfer of heat by radiation can be represented by an equation of the same form as that for the conduction of heat in a solid. If T is the temperature at height z

$$\frac{\partial T}{\partial t} = K_R \frac{\partial^2 T}{\partial z^2}, \tag{1}$$

where K_R is a constant for which the name "radiative diffusivity" was suggested. It is of the order of magnitude of 10^3 in C.G.S. units.

In the same paper it was shown that the vertical transfer of heat by the action of eddies can be represented by a similar equation

$$\frac{\partial T}{\partial t} = K_E \frac{\partial^2 T}{\partial z^2}, \quad (2)$$

where K_E is the eddy diffusivity, whose order of magnitude varies from zero to 10^6 in C.G.S. units.

It is assumed in the derivation of these equations that K_R and K_E do not vary with height. This is admittedly true only to a first approximation. The joint effects of radiation and turbulence may be represented by the single equation

$$\frac{\partial T}{\partial t} = (K_R + K_E) \frac{\partial^2 T}{\partial z^2}. \quad (3)$$

It follows that the examination of thermal records of any kind cannot yield a direct estimate of either K_E or K_R separately, but can only give their sum $K_E + K_R$. We know, however, that the order of magnitude of K_R cannot exceed 10^3 , and if the sum $K_E + K_R$ comes out much greater than this, say of order 10^5 , we may take this value to be K_E , since only a small fraction of it can be accounted for by K_R .

3. *The Upward Transfer of Changes of Surface Temperature.*

G. I. Taylor has discussed* the upward transfer of changes of surface temperature by eddy motion. His analysis can be used in conjunction with equation (3) above to treat the combined effects of radiation and turbulence. Taylor discussed two cases:—

- (a) The surface temperature changes uniformly at a rate $p^\circ \text{C. per second}$, so that the surface temperature at time t is $T_s = T_0 + pt$.
- (b) The temperature of the surface layer changes suddenly from T_s to T'_s , and afterwards remains constant.

We shall suppose that initially the lapse-rate is constant at all heights, so that $T = T_s + \beta z$. We introduce a variable ζ given by

$$\zeta^2 = z^2/4 (K_R + K_E) t.$$

* 'Phil. Trans.,' A, vol. 215, pp. 1-26 (1915).

Case (a).—The appropriate solution is

$$\begin{aligned} T &= T_s + \beta z + pt [(1 + 2\zeta^2)(1 - \operatorname{erf} \zeta) - 2\pi^{-\frac{1}{2}} \zeta e^{-\zeta^2}] \\ &= T_s + \beta z + pt \psi(\zeta), \text{ say.} \end{aligned} \quad (4)$$

Taylor shows that at $\zeta = 0.8$ $\psi(\zeta) = 0.1$, so that the effect of the variation of surface temperature is negligible beyond the height corresponding to $\zeta = 1$, i.e., beyond the height given by

$$z^2 = 4 (K_R + K_E) t. \quad (5)$$

Case (b).—The appropriate solution is

$$\begin{aligned} T &= T_s + \beta z + (T'_s - T_s)(1 - \operatorname{erf} \zeta) \\ &= T_s + \beta z + (T'_s - T_s) \chi(\zeta). \end{aligned} \quad (6)$$

$\chi(\zeta) = 0.1$ when $\zeta = 1.16$, and $\chi(\zeta) = 0.16$ when $\zeta = 1.0$, and we may again assume with Taylor that at heights beyond those given by $\zeta = 1$, or

$$z^2 = 4 (K_R + K_E) t, \quad (5)$$

the effect of the upward diffusion of heat is negligible. Taylor used equation (3) with K_E instead of $K_R + K_E$.

These results were used by Taylor to deduce the values of K_E , from the observations of the heights at which pronounced bends in the temperature-height curves were found to occur.

If we assume a value 10^5 for $K_R + K_E$, corresponding to fairly turbulent conditions, K_E being greatly in excess of K_R , then the height to which a surface change of temperature is transmitted in t seconds is given by $z^2 = 4 \cdot 10^5 t$, or $z = 2 \cdot 10^2 \sqrt{10t}$ where z is in centimetres. The height in metres is given by $z = 2\sqrt{10t}$, so that in 10 seconds the greatest height to which a disturbance of surface temperature is transmitted is 20 metres.

The result is most simply seen from the following table :—

Depth of heated layer.	$K_R + K_E = 10^5.$	$K_R + K_E = 10^6.$	$K_R + K_E = 650.$
50 cm.	0.008 sec.	0.6 sec.	1 sec.
1 metre	0.025 "	2.5 "	4 "
5 "	0.625 "	1 min.	100 "
10 "	2.5 "	4 "	6½ min.
30 "	22.5 "	37 "	60 min. = 1 hour
100 "	250 "	400 "	11 hours

It is of interest to apply these results to discuss the effect of the sudden appearance of the sun from behind a cloud. The ground and the air in contact with it are raised to a higher temperature almost instantaneously, and the temperature of the surface remains afterwards fairly constant, so that the phenomena can be discussed under case (b) above.

We may use equation (5) to determine the lag in the rise of temperature at different heights. The time $t = z^2/4(K_R + K_E)$ is about equal to the interval which should elapse between the initial rise in temperature at the ground and at height z . The time so deduced will vary within very wide limits as $K_R + K_E$ is very variable. Instrumental records are seldom available in a suitable form to determine t with any degree of accuracy. In addition no instrumental records are available giving the time of commencement of sunshine after cloud with accuracy. If the times t_1 and t_2 for commencement of the rise of temperature at heights z_1 and z_2 are available, the value of $K_R + K_E$ is readily seen to be

$$(z_1^2 - z_2^2)/4(t_1 - t_2),$$

and it is possible that this method might be adopted in some cases to measure $K_R + K_E$. The method can only yield useful results when the time difference $t_1 - t_2$ is fairly long, say, at least 10 minutes.

When only radiation is effective, conditions being initially very stable with no turbulence, $K_R + K_E$ must be replaced by K_R . We shall adopt as the value of K_R the figure 650, a value found to correspond closely with average conditions.

If now the ground is heated, either suddenly by the appearance of the sun from behind a cloud, or gradually by the normal continued action of the sun, the depth of the layer at the ground which has become heated at time t is given by

$$z = \sqrt{4K_R t} = 50t^{\frac{1}{2}} \text{ centimetres.}$$

The depth of heated layer for different intervals of time is given in the last column of the table above.

It will be noted that the effects of radiation are limited to a shallow layer near the surface, since the layer affected by surface changes only extends up to 100 metres in 12 hours. The major diurnal changes of temperature in the upper air cannot therefore be regarded as due to radiation transmitted from the ground upwards.

This is confirmed when we investigate the diurnal changes of temperature

on the basis of equation (5) above. The solution of this equation which corresponds to the boundary condition of a diurnal curve of temperature

$$T = A \sin (2\pi t'/24)$$

(where t' is measured in hours) at the ground is

$$T = Ae^{-bz} \sin (2\pi t'/24 - bz)$$

Here

$$b^2 = \pi/24(K_R + K_E) \times 60 \times 60.$$

If we neglect K_E , and let $K_R = 650$, we shall obtain the relation corresponding to radiation acting alone.

$$b^2 = \pi/24 \times 650 \times 3600 \quad \text{and} \quad b = 2.4 \times 10^{-4}.$$

The amplitude of the diurnal variation of temperature will have fallen to $1/e$ of its surface value at a height given by $bz = 1$ or $z = 4000$ cm. It will have fallen to $1/10$ th of its surface value at a height of 100 metres, and to $1/100$ th of its surface value at a height of 200 metres. The time of maximum at a height of 40 metres would be retarded by nearly 4 hours, that at 100 metres by nearly 9 hours, and that at 200 metres about $17\frac{1}{2}$ hours, after the time of maximum temperature at the surface.

The effects of radiation alone are therefore only of importance in the layer in immediate contact with the surface of the earth, and the large scale variations of temperature with height cannot be explained as purely radiational effects.

In this discussion it has been assumed that all radiation is either completely absorbed or completely unabsorbed in a layer containing 0.3 mm. of precipitable water. The effect of the presence of radiation which is only partially absorbed will modify to some extent the results derived here, and may cause the estimated depth of the heated layer to be in error by a fraction of the computed depths. For the discussion of meteorological phenomena and the general question of the stability of the lower atmosphere, a small error in z is not of serious consequence.

4. *The Formation of Nocturnal Inversions.*

The radiation from the ground to a clear sky at night rapidly cools the surface and consequently the air in contact with the surface. The spreading upward of this cooling effect can be treated by the method of § 3 above. The temperature of the air in immediate contact with the ground will be assumed to fall at a uniform rate p° C. per second. Then we may use equation (4) above, with the sign of p changed. The table given in § 3 will now give the

height to which the radiative cooling extends in a given time, and the effect of radiation acting alone is given by the figures in the last column. It is seen that the inversion of the lapse-rate at the ground extends to 30 metres in 1 hour, to about 42 metres in 2 hours, to 60 metres in 4 hours, and to 100 metres in 11 hours. These figures are roughly in accordance with such observations as are available. N. K. Johnson* has described in some detail the observations at Porton up to a height of 17 metres above the ground. With the mean value of K_L we have adopted, the inversion should extend to 17 metres in about 20 minutes, and this is of the same order as the times yielded by Johnson's observations. It will probably be found that inversions grow rather more rapidly than might be expected from the figures derived above, since in practice there is always some turbulent motion in the atmosphere, particularly in the early part of the night. But the observed growth of nocturnal inversions agrees much more closely with the theoretical result with radiation acting alone than the growth of large lapse-rates during the day time.

The figures derived above were communicated privately to Major A. R. Low, of the Air Ministry, and furnished the necessary physical basis for numerical application of the criterion for instability of a layer of atmosphere heated from below, both for the critical solution and for multiple solutions of the differential equation involved.† These multiple solutions involving more than one circuit of motion in the depth of the layer appear to be capable of explaining the existence and persistence of super-adiabatic lapse-rates. Major Low's discussion of this question is being presented to the third International Congress for Technical Mechanics at Stockholm, August, 1930.

* Johnson, "A study of the Vertical Gradient of Temperature in the Atmosphere near the Ground," 'M.O. Geophysical Memoir,' No. 46 (1929).

† 'Proc. Roy. Soc.,' A, vol. 125, pp. 180-195.

Extended Energy Functions of the Hydrogen Molecule.

By P. M. DAVIDSON, Ph.D., and W. C. PRICE, B.Sc., University College,
Swansea.

(Communicated by O. W. Richardson, F.R.S.—Received October 16, 1930.)

The potential energy U of a diatomic molecule will be here defined as the work which must be done on the nuclei in order to alter their separation slowly from its equilibrium value r_0 to its actual value r . It is usually expressed as a power series in ξ , a quantity defined as $(r - r_0)/r_0$. The number of terms of this series which can be evaluated with reasonable accuracy depends on the particular spectrum, and the series represents the potential energy correctly for a greater or less range on either side of the equilibrium position; but it becomes quite incorrect both at very small distances, where it should approach infinity, and at very large distances, where it should tend to a constant value asymptotically. For the various states of hydrogen such series have been calculated by Richardson and Davidson in "The Energy Functions of the Hydrogen Molecules."*

An attempt to represent potential energies throughout a greater range has recently been made by Morse,† who shows that if the potential energy, on the above definition, were given by

$$U = D [1 - e^{-a(r-r_0)}]^2, \quad (1)$$

D and a being constants, then the vibrational energy levels would be of a simple and frequently occurring type, being expressed by

$$E_n = (2D/\mu)^{1/2} (a\hbar/2\pi) (n + \frac{1}{2}) - (a^2\hbar^2/8\pi^2\mu) (n + \frac{1}{2})^2 \\ = \hbar\omega_0 (n + \frac{1}{2}) - \hbar\omega_0 x (n + \frac{1}{2})^2, \quad (2)$$

where ω_0 is the frequency for infinitesimal amplitude, and $\omega_0^2/4\omega_0x = D/\hbar$. If D is "expressed as a frequency," the right-hand side of this last equation becomes simply D , and the equation is then unaltered if everything is expressed in wave-numbers. U goes asymptotically to a constant value D at $r = \infty$, as it should do; and Morse shows that though it does not actually go to infinity as r goes to zero, yet in most cases it goes to a decidedly large value.

Fues‡ has shown that if U is represented by a series expansion all levels

* 'Proc. Roy. Soc.,' A, vol. 125, p. 23 (1929).

† 'Phys. Rev.,' vol. 34, p. 1 (1929).

‡ 'Ann. Physik,' vol. 80, p. 367 (1926).

which can be interpreted on the old mechanics can be interpreted also on the new theory. Morse's calculation employs the wave mechanics, and if instead the old mechanics is applied to equation (1), the expression for E_n is obtained from (2) on replacing $n + \frac{1}{2}$ by n throughout. It is hardly legitimate to deduce this directly, for all integral values of n , from the formulæ of Fues, but an independent proof can easily be given. The quantum condition is

$$\oint p_r dr = \oint (2\mu)^{\frac{1}{2}} [W - U(r)]^{\frac{1}{2}} dr \\ = \oint \left[-\frac{(2\mu)^{\frac{1}{2}}}{ax} \{ -(D - W) + 2Dx - Dx^2 \}^{\frac{1}{2}} dx \right] = nh, \quad (3)$$

in which the substitution $x = e^{-a(r-r_0)}$ has been made. Considering the Argand diagram, the path is a loop lying along the real positive axis, with one of its extremities between 0 and 1, and the other between 1 and 2. The required integral is the difference of two terms, obtained by taking the integration round two paths, the first a small circle about the origin, the second a circle at infinity. The first integral is obtained immediately from the residue of the integrand at the origin, and the second in a similar manner after making the usual substitution $y = 1/x$. Giving the terms their correct signs, rearranging and squaring, we have

$$D - W = [(anh/2\pi\sqrt{2\mu}) - \sqrt{D}]^2$$

from which we find at once that the value of the quantised energy W is identical with the expression (2) for E_n , with $n + \frac{1}{2}$ replaced by n throughout.

For hydrogen, unfortunately, the inaccuracy of U curves drawn from the Morse formula is probably appreciable. In the first place, the inherent failure for small values of r is here rather marked, especially in $2^1\Sigma$, for which, using Morse's figures, the value of expression (1) at $r = 0$ is only a little over $2D$, instead of infinity. In the second place, the formula is only applicable if the vibrational energy levels are represented fairly accurately by (2), and for some states of hydrogen this is by no means true; thus the value of D , obtained by extrapolating the first two vibrational levels of $2^1\Sigma$, differs considerably from the value obtained by extrapolating the whole series of the known levels.

It is therefore interesting to see whether, for this simple molecule, a U -formula cannot be derived from a separate consideration of all the forces from which it arises. Imagining the nuclei held at a given separation, we have firstly the repulsion between them; the force inwards on each is $-e^2/r^2$. Consider now one of the electrons. At a given instant it exerts a force on

each nucleus; the arithmetical mean of the components, measured inwards, along the internuclear axis, will be called the "effective force of the electron," and its time-average the "mean effective force of the electron," say f_1 for the one electron and f_2 for the other. Now the internuclear component, measured inwards, of the force which the electronic system exerts on one nucleus must be equal, in a time average, to that which it exerts on the other; for the principle of action and reaction shows that otherwise the centre of gravity of the electrons would not be remaining in the vicinity of the nuclei. This force is thus, by definition, the sum of the two "mean effective forces" of the electrons. Thus when the nuclear separation is increased by dr an amount of work $(f_1 + f_2) dr$ has to be performed against the electronic forces, whether one or both of the nuclei be moved. The total work which has to be done is $\{f_1 + f_2 - (e^2/r^2)\} dr$, and integration gives

$$U = (e^2/r) + \int f_1 dr + \int f_2 dr + C, \quad (4)$$

the constant being chosen so as to make U zero at $r = r_0$.

To see how f_1 and f_2 vary with r , consider one of the electrons, and let the nuclei be close together, so that their separation dr is small compared with the distance x of the electron from the centre of the nuclear axis. If the angle between the directions of dr and x is θ , the effective force of the electron is

$$\frac{1}{2}e^2x^{-3}(1 - 3\cos^2\theta)dr. \quad (5)$$

Thus the effective force changes from an attraction to a repulsion as θ passes through 55° , for which angle $\cos^2\theta = \frac{1}{3}$. The force is proportional to dr , and vanishes when the nuclei come together. Now if, in the actual molecule, the nuclei, initially together, are drawn slowly apart through a small distance dr , the variation in the electronic orbits will in general be small, so that the mean effective force of each electron will be proportional to dr (unless the multiplier of dr in (5) happens to have a mean value zero for this electron's orbit). We conclude that if, say, f_1 is plotted against r , the curve starts from zero at $r = 0$ with a slope which is generally finite. It returns to zero asymptotically at $r = \infty$, for at that stage we have two hydrogen atoms, and the force on a nucleus due to the distant atom is vanishing, and so is the force needed to hold the nuclei apart; hence the mean force on the nucleus due to the adjacent electron is also vanishing; thus the mean effective force of that electron vanishes.

A simple function having all the properties required for the mean effective force is are^{-ar} , and if we replace the factor ar by a power series in r , we may

hope to get a good approximation. It may not give quite the correct type of asymptotic approach to zero as $r \rightarrow \infty$, (possibly it should fall off as a finite negative power); but the numerical error should everywhere be small. U expressed in volts has now the form

$$U = (A/\rho) + \int_n (a_n \rho^n e^{-\alpha \rho} + b_n \rho^n e^{-\beta \rho}) d\rho + C. \quad (6)$$

Here $\rho = r/r_0$, $A = 26.9 \times (r_H/r_0)$, r_H being the radius of the first circular Bohr orbit of the hydrogen atom. The values of f_1 and f_2 corresponding to (6) may conveniently be expressed as multiples of (e^2/r_H^2) , the force between the nucleus and electron in the first Bohr orbit of hydrogen. The value of f_1 is

$$0.037 \times (r_H/r_0) e^{-\alpha \rho} \sum_n a_n \rho^n \quad (7)$$

and f_2 is obtained by changing a and α to b and β .

Considering only the first two terms of each summation (n equal to 1 and 2) we have on integration

$$U = (A/\rho) - e^{-\alpha \rho} [A_1(1 + \alpha \rho) + A_2(2 + 2\alpha \rho + \alpha^2 \rho^2)] - \dots + D \quad (8)$$

Here $A_1 = a_1/\alpha^2$, $A_2 = a_2/\alpha^3$, and similarly for B_1 and B_2 ; the dots indicate that the expression involving β , B_1 and B_2 is omitted, its form being obvious. The constant C is replaced by D , since its value is evidently $U(\infty)$. The values of A and D are known for every molecular state,* and the normal procedure for determining the other constants would be to find an expression for the quantised energy levels permitted by (8). It will appear, however, that for the accuracy which we shall here employ, the same result can be had by expanding (8) as a series in ξ for the neighbourhood of $r = r_0$, and comparing the coefficients with those found by Richardson and Davidson. Those series employ the old mechanics, but, as explained there, the corresponding formulæ on the wave mechanics are easily found; since the coefficients are only altered by a few per cent., we shall here use the old mechanics. It is to be remembered also that the first two or three terms of each series may be taken as fairly accurate, later terms being liable to an increasingly large error. The conditions to determine the constants are then:—

(1) As $r \rightarrow 0$ the expression for U becomes $\{(A/\rho) - (A_1 + 2A_2 + B_1 + 2B_2) + D + \text{vanishing terms}\}$. The value of the bracketed constant is known, since the electronic orbits become those of the helium atom.

(2) In the expansion in powers of ξ the constant term is zero.

(3) The coefficient of ξ is also zero.

* *Loc. cit.*

(4), (5), (6) The coefficients of ξ^2 , ξ^3 , ξ^4 , ..., are those found by Richardson and Davidson.

We begin with the first approximation, setting $A_2 = B_2 = 0$ in (8); that is, for each electron we take only the first term of the series for the mean effective force. We will determine the values of A_1 , B_1 , α and β from the conditions (2), (3), (4) and (5). Whether the result is a good approximation may be judged by the extent to which the other conditions are satisfied.

For the level which they called 2^3S , and which is now called $2s^3\Sigma$ in the standard nomenclature,* Richardson and Davidson find

$$U = 6.24\xi^2 - 10.2\xi^3 + 12.1\xi^4 - 13.4\xi^5 + 15\frac{1}{2}\xi^6 \dots \quad (9)$$

The conditions which we are using thus ensure the vanishing of the constant and the coefficient of ξ , and the values 6.24 and -10.2 for the coefficients of ξ^2 and ξ^3 . We find $A_1 = 17.05$, $B_1 = 20.7$, $\alpha = 3.482$, $\beta = 1.05$. These give a series

$$U = 6.24\xi^2 - 10.2\xi^3 + 13.4\xi^4 - 15.6\xi^5 + 16.3\xi^6 \dots$$

The bracketed constant in condition (1), which is here simply $A_1 + B_1$, has a value $37\frac{1}{2}$. It should be 42. This means that the sum of the areas of the f_1 and f_2 curves over the whole range $r = 0$ to $r = \infty$ is less than the true area by about one-tenth of its amount. The area in the range r_0 to ∞ is correct, for this is the condition (2); the error is in the range 0 to r_0 , where the area is too small by about one-sixth of the true value. These results are satisfactory for a first approximation; in fact, the inaccuracy of the later terms in (9) would make a further approximation on their account unjustifiable.

For 2^1S , now called $2p^1\Sigma$, Richardson and Davidson found $A = 10.9$, and

$$U = 2.84\xi^2 - 4.63\xi^3 + 7.46\xi^4 - 11.6\xi^5 + \dots$$

and the above procedure leads to $\alpha = 3.891$, $\beta = 0.875$, $A_1 = 18.75$, and $B_1 = 16.00$, giving

$$U = 2.84\xi^2 - 4.63\xi^3 + 8.0\xi^4 - 11.3\xi^5 + \dots$$

and for $A_1 + B_1$ the value $34\frac{1}{2}$ instead of 41, so that the total area of the f_1 and f_2 curves is less than the true area by about one-seventh of its amount.

For 3^3P , now called $3p^3\Pi$, Richardson and Davidson found

$$U = 5.37\xi^2 - 8.36\xi^3 + 8.46\xi^4 - 8.38\xi^5 + \dots$$

* Richardson has given a diagram of all the molecular states in 'Proc. Roy. Soc.,' A, vol. 126, p. 487.

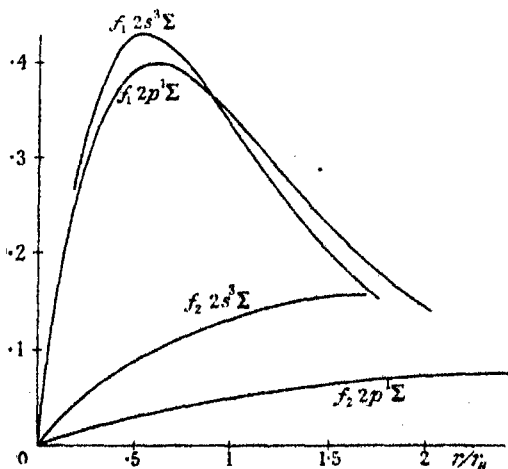
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The value of A is 13.5 , so that the last two terms of the U series are numerically smaller than would be expected by analogy with the other states. A fairly good general agreement is given by $\alpha = 4.3866$, $\beta = 1.14$, $A_1 = 18.5$, $B_1 = 21.8$, giving

$$U = 5.37\xi^2 - 7.3\xi^3 + 9.5\xi^4 - 12.6\xi^5 + \dots$$

and for $A_1 + B_1$ a value 40.3 instead of 38 . The total area of the force curves is thus a little too great.

It thus appears that the method is satisfactory for the primary purpose of finding a U formula which shall be fairly correct throughout the whole range, and we may conclude that the curve of $(f_1 + f_2)$ gives a fair representation of the mean force which the electronic system exerts on either nucleus. There is, however, no evidence that each f may really be regarded as the mean effective force of one electron; this, in fact, seems too much to expect. The curves are shown in the figures using the units of force specified above. The great difference between f_1 and f_2 is a point in their favour; for we are dealing essentially with an inner and an outer electron, and on account of the factor x^{-3} in (5), together with the comparatively slow variation with θ , we see that if the orbits are at all similarly orientated the f of the *inner* electron is likely to be very much the greater for small values of r ; that is, its curve will have the steeper rise from zero at $r = 0$. It is also likely to attain a larger maximum. Accordingly f_1 should be given to the inner and f_2 to the outer electron.



Summary.

Previous formulæ for the potential energy of a diatomic molecule are, from their nature, valid for only a limited range of the internuclear distance, failing either at small distances, or at large distances, or both. An attempt is here made to derive a formula applicable to the full range. This formula appears as the sum of two series, and for the various states of hydrogen it is shown that even if only the first term of each series is taken the formula satisfies, approximately, all the conditions which are required of it. The significance of the two series is discussed in terms of the forces between the components of the molecule.

On Optical Pyrometry.

By A. C. EGERTON, F.R.S., and M. MILFORD.

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The most convenient and accurate instrument for the measurement of high temperatures is undoubtedly the disappearing filament pyrometer.* During some work on the vaporisation of palladium and nickel, Mr. C. W. Gibby and one of the present authors had occasion, some years ago, to design a modification of this pyrometer, so as to magnify small filaments of these metals, which were heated to incandescence electrically. Recently, having undertaken investigation of the carbon arc at high pressures, the methods of pyrometry then used have been extended, with the object of diminishing some of the difficulties connected with optical pyrometry.

The first difficulty is that the readings of the ordinary optical pyrometer are not independent of the distance, when sighted on a small source, such as a filament, for the reason that the cone of rays from the source does not fill the exit aperture completely. It is therefore essential to magnify the source of light. It is unnecessary to describe here the magnifying pyrometer which was constructed, because the design of the optical part of the instrument is similar to that detailed by Fairchild and Hoover,† and the position of the diaphragms and lenses for good definition agreed with those specified by those authors,

* Holborn and Kurlbaum, 'Ann. Physik,' vol. 10, p. 225 (1903); Burgess, 'Bull. Bur. Stds.,' vol. 1, p. 189 (1904).

† 'J. Amer. Opt. Soc.,' vol. 7, p. 543 (1923).

although arrived at independently of their recommendations. Provision was made for two different magnifications by removal of the front component of the objective lens, the latter being at a fixed distance (35 cm.) from the lamp. When investigating the temperature distribution over a small source, it is very convenient to be able to suit the magnification to the size of the object or the bounds of the working distance. The working distance for the higher magnification ($\times 20$) was 20 cm., and with the front combination removed about 45 cm. As a precision instrument, the magnifying pyrometer* has advantage over an ordinary optical pyrometer, because it can be sighted on a source which, being smaller, is more easily maintained at a uniform and constant temperature.

For the work on vaporisation from filaments, a Corning red screen and sectors to cut down the light intensity were quite satisfactory; temperatures above 2000° K. were not involved. But for measurements of arc temperatures (3500° K. and upwards), corrections have to be made for the change in "effective wave-length"† of the red glass in combination with the approximately "neutral" absorption screens which are employed to diminish the intensity of the light source. The determination of these corrections has been discussed in detail by various authors,‡ notably by Hoffmann. Screens have been found whose absorption changes with wave-length in such a way as to compensate for the variation in spectral intensity of the source as the temperature changes. These adjustments and corrections, which may amount to about 50° at 3500° K., become unnecessary if the intensity match could be made under monochromatic conditions. The spectral pyrometer of Henning§ effects this, but the instrument is more cumbersome than the pyrometer alone and the slit width is such that a band at least 100 Å. broad is used. Pirani|| suggested the use of dyed filters, such as Wratten ϵ'' green, transmitting from about 5100 to 5700 Å. The effective wave-length changes only by 1 per cent. for a temperature rise from 1000° to 4000° instead by of as much as 3 per cent. for the red glass

* Henning and Heuse, 'Z. Physik,' vol. 29, p. 157 (1924); Forsythe, 'Astrophys. J.,' vol. 43, p. 295 (1916).

† Foote, 'Bull. Bur. Stds.,' vol. 12, p. 483 (1916).

‡ Hoffmann, 'Z. Physik,' vol. 17, p. 1 (1923); Hyde, Cady and Forsythe, 'Astrophys. J.,' vol. 42, p. 294 (1915); Forsythe, 'Trans. Faraday Soc.,' vol. 15, Part 3, p. 21 (1920); Henning, 'Z. Physik,' vol. 30, p. 285 (1924).

§ 'Z. Inst. Kunde,' vol. 30, p. 61 (1910); cf. Mendenhall, 'Phys. Rev.,' vol. 33, p. 74 (1911).

|| 'V. Deut. Phys. Ges.,' vol. 15, p. 826 (1913); cf. Hoffmann, 'Z. Inst. Kunde,' vol. 41, p. 170 (1921).

(Jena F. 4512). Pirani also pointed out the advantage of using a green screen, since the eye's sensitivity is a maximum at 5600 Å. The permanency of dyed filters, however, would be questionable.

For the present purpose, a special composite glass filter was devised. Use was made of the sharp edge of an absorption band of a "didymium" glass (Jena B.G. II) at about 5750 Å. The small region between that edge and that of a band at 5550 Å. in the green glass (V.G. 3) is transmitted with little absorption. The region is still further narrowed and the rest of the spectrum eliminated by means of an orange glass (O.G. 2). A green glass (V.G. 1) completes the absorption of the red regions. The various glasses are cemented together with balsam; the transmission curves for the several glasses are given in fig. 1. The transmission of the composite glass is given by the full

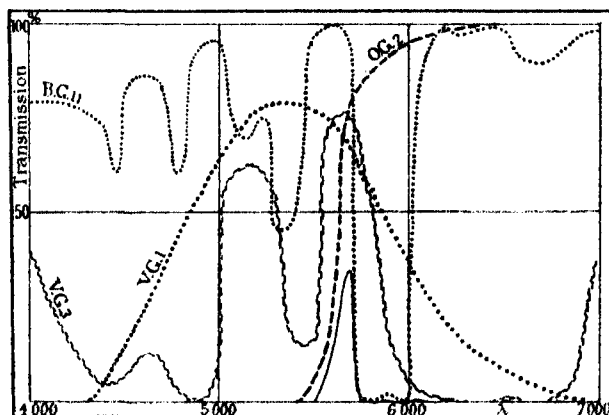


FIG. 1.

line. A band of light 130 to 140 Å. in visible width is transmitted between 5740 and 5600 Å.; the greater part of the energy (about 70 per cent.) is within the region 5670 ± 25 Å. Thus a filter is obtained as monochromatic as is needed to avoid appreciable errors arising, when extrapolating by the aid of Wien's equation from regions of temperature in which the pyrometer can conveniently be calibrated, up to arc temperatures. The change in the spectral absorption of the "neutral" glasses was found too small over such a narrow band to require correction. The filter transmits in the region of maximum sensitiveness of the eye, and furthermore, extrapolation by Wien's equation (in distinction to Planck's) is valid to a higher temperature in green light than in red. Temperatures below 1100° C. cannot be conveniently measured with such a composite filter, but it is hoped to make a simpler filter on similar

lines which will transmit more light. (The filter described lets through some light in the region 6100 Å., but it is so small a fraction of the total that it does not contribute sufficient to affect the calibration of the pyrometer.)

The next trouble with an optical pyrometer is its calibration. For this purpose, knowing λ the wave-length (or "effective wave-length"), c_2 , Wien's constant (1.432 cm. per degree) and T_1 the temperature of melting gold, the Wien equation is used,

$$\log \frac{H_1}{H_2} = \frac{0.4343 C_2}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where H_1/H_2 is the ratio of the intensities of the images of the source, having the same brightness as a blackbody at T_1 and T_2 respectively. A blackbody source is essential unless the brightness temperature or the reflection coefficient of the source is known.* If the pyrometer can be compared with the readings of an instrument which has already been standardised against a blackbody at known temperatures, then inter-comparisons on the same lamp can be made, but primarily measurements must be made on a blackbody. A blackbody furnace is costly, and the difficulty of obtaining uniform temperature considerable. Furthermore, the working distance of a magnifying pyrometer is often too small for convenient observation of the temperature of such a furnace. Mendenhall† first suggested the use of an electrically heated wedge as a blackbody source, and showed that for a wedge of 10° , with reflecting surfaces made of platinum, the emission is 99.8 per cent. black. He also showed that for the thin metal used, the outside temperature was within a fraction of a degree of the inside. It is possible to determine the outside temperatures by watching the melting of small pieces of metals (*e.g.*, gold, nickel, palladium, etc.) of known melting point placed on the outside.‡ A blackbody source easy of construction is thus available, upon which a magnifying pyrometer can be standardised. The arrangement used in the present work is shown in fig. 2 (plan and elevation). The wedge is formed of platinum foil (0.001 cm. thick) on the part A; it is slid into position and clamped by the shaped plates B_1 and B_2 . The wedge measures 5×0.5 cm., the angle being 10° . The block B_1 , running on guides, is fitted with a spring attachment, so that the wedge is kept under slight tension and maintains its shape when heated. The holder fits into a tube and concentric rod, insulated from each other, and carried by the ground cap of

* Henning, 'Z. Electrochem.', vol. 30, p. 309 (1924).

† 'Astrophys. J.', vol. 33, p. 91 (1911).

‡ Burgess and Waltenburg, 'Bull. Bur. Stds.', vol. 11, pp. 41, 591 (1915).

the glass vessel. Connection with the current supply is made at C_1 and C_2 ; a current of 10 amps. suffices for $1300^\circ \text{ K. in vacuo}$. The wedge can be heated

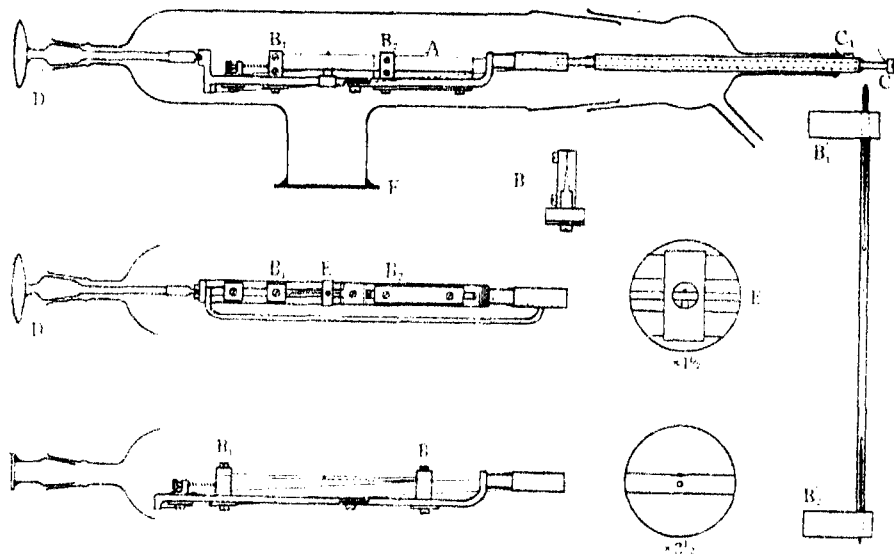


FIG. 2.

in a high vacuum or, in the case of metals which volatilise at their melting points, in hydrogen or argon. Observations are made through the window F , the correction for which is known. By means of a pointer behind the wedge and a small aperture in front (E), the portion of the wedge on which the pyrometer is sighted can be ascertained, and by turning the cap D the back of the wedge can be accurately aligned. The small piece of pure metal ($\frac{1}{2} \text{ mm.} \times 1/10 \text{ mm.}$) cut from wire is placed on the upper surface of that part of the wedge on which the pyrometer is sighted and within 1 mm. of the back edge. The melting of the metal is observed through a microscope. The temperature of the wedge is gradually raised till the sample just melts, the current being then held constant while observations are made with the pyrometer. The adjustable mercury-carbon resistance* was found very convenient for this purpose.

The method is not free from difficulties. First, there is the blackness condition. Although a burnished wedge of platinum of 10° should provide a satisfactory blackbody, the surface tends (owing to crystallisation) to become less regularly reflecting and the shape of the wedge, particularly the sharpness of the back edge, may become impaired on extended use. Secondly, there is

* Egerton and Milford, 'J. Sci. Inst.,' vol. 7, p. 299 (1930).

the question whether the sample is at the temperature of the blackbody observed. Conduction provides that the outer surface temperature is very nearly the same as the inner, but whether the sample placed on the surface is at the same temperature as the surface is another matter, because the presence of the sample alters to some extent the electrical conductivity in its neighbourhood and also the reflection coefficient, and consequently the emission from that region will be different. Another possible difficulty is that if the lower surface of the sample alloys with the platinum below its melting point, collapse of the sample below the true melting point might occur. In point of fact, none of these errors is serious; by altering the size of the sample, by placing it on patches where the metal has been previously melted, by changing the thickness of the wedge and by other tests, it is shown that the errors are more important which arise from variation of blackbody condition, of position and good contact of the sample on the wedge and also from observation of the temperature. There is a considerable temperature gradient across the wedge (40° at 1300° K.) and it is necessary to place the sample in the position of maximum temperature. Good contact with the strip is essential; occasionally an adsorbed gas film appears to be locked between the sample and the wedge, the former looking black against the bright background; then suddenly contact is gained and the sample becomes bright. Melts take place quite suddenly, but it is important to raise the temperature very slowly near the melting point. It is interesting to note the bright green appearance of the freshly molten gold, the black pool of molten silver and the bright nickel melt. All the errors, except lack of blackness, tend to give a high result for the melting temperature.

The following illustrate the agreement obtained for the gold melting point with a certain wedge:—0.663, 0.662, 0.660 volts (0.001 volt equivalent to 1° C.). The nickel point gave results agreeing within $\pm 5^\circ$, but the results for palladium, owing chiefly to vaporisation, which makes it necessary to raise the temperature rather quickly, were not so satisfactory. The method has been applied to determine the melting point of other metals (*e.g.*, iron, which has to be carried out in pure hydrogen).

Mendenhall and Forsythe* have employed the wedge method for the determination of reflection coefficients of the metal of which the wedge is constructed; the apparatus here described is particularly convenient for the purpose, the wedge being turned so as to view the cavity and the outer surface alternately.

Owing to the variability of the wedge as a blackbody source, another type

* 'Astrophys. J.,' vol. 37, p. 380 (1913).

of blackbody was arranged, consisting of a tube of platinum (1.4 mm. external diameter $\times$ 10 cm. long $\times$ 0.15 mm. thick), with a small hole (0.3 mm.) in the wall at the middle. The tube is mounted in the same arrangement, except that blocks (B_1' and B_2' in fig. 2) suitable for clamping the tube were substituted for the V-shaped blocks. Worthing has used a hollow filament of tungsten punctured with small holes in order to measure the variation of reflection coefficient with λ or T , and has discussed the various possible sources of error.*

By flattening slightly the upper side of the tube above the hole (see magnified view) small samples could be melted as before, and the results obtained were better than for the wedge, *e.g.*, for the nickel point (*a*) 1453°C. ; (*b*) 1452°C. ; (*b*) 1453°C. for two different samples (*a*) and (*b*) of pure nickel.

Not being satisfied, for the reasons already given, that the sample placed outside is actually at the true temperature of the blackbody, the tube was arranged differently (see fig. 2). The same platinum tube was placed vertically, and a small piece of silica was tapered so as to fit centrally into the upper end of the tube, with its lower end shaped as a hook. To this is attached a piece of wire (diameter $1/10$ mm.) of the metal whose melting point is required; to the other end of the wire is affixed by a hook a small silica bob ($1/50$ gram), which just keeps the wire central, but is too light to stretch it. The wire is of such a length that it is in that portion of the blackbody in which the temperature is constant and it receives heat by radiation within the blackbody. The wire is almost invisible when the hole is observed through the pyrometer. The temperature of the tube is raised very slowly until the temperature is reached when the wire collapses and the bob drops down. The method is simple and the wire cannot be contaminated. It might also be used to investigate expansion and other properties at high temperatures.

For palladium, the results of two trials by this method gave 1.435 and 1.435 volts ± 0.01 , corresponding with 1555°C. on the curve obtained from observations at the gold point and at the nickel point and by checking the curve so obtained by the rotating sector method.

Although once the blackbody brightness S_1 is known at a fixed point T , it is possible to construct the calibration curve of the pyrometer by observations on a Tungsten strip lamp, using sectors of known angle to diminish the intensity by a known amount, yet it is convenient to be able to check such a calibration by observations at other fixed points on a blackbody. The methods outlined above enable this to be done, and a magnifying pyrometer, together with such

* Worthing, 'Phys. Rev.', vol. 10, p. 377 (1917).

simple apparatus, might perhaps provide an alternative to the more costly equipment to establish the scale of the ordinary optical pyrometer.

As in the case of the resistance thermometer, where the naphthalene point forms a convenient secondary standard point between the sulphur and water boiling points, so for the optical pyrometer it is convenient to have secondary fixed points, like the nickel melting point, and it is suggested that a point between this and the gold point would be useful as provided by the melting of the alloy of nickel and palladium (55 per cent.) about 1265° C.

Once the primary calibration curve is fixed for the range from the gold point to the palladium point, it is an easy matter to determine the constants for the absorption screens. For this purpose, the Tungsten strip lamp is used as a source which can be maintained constant at fairly high temperatures, and since the colour filter is monochromatic, the absorption coefficients do not vary with the temperature of the source observed, and it can safely be assumed that the screens are additive. The curves can then be drawn for each grouping of glasses up to 5000° K. or higher, enabling the (brightness) temperature to be read directly.

It is an advantage to provide two monochromatic glasses for the pyrometer, as observations can then be made in two wave-lengths at a definite temperature; since

$$\frac{1}{\tau} = \frac{1}{\lambda_2 - \lambda_1} \left[\frac{\lambda_2}{s_1} - \frac{\lambda_1}{s_2} \right],$$

where S_1 and S_2 are the blackbody temperatures (as measured by the current through the pyrometer filament corresponding to λ_1 and λ_2), τ , the colour temperature, can be determined, as Henning has pointed out, provided the brightness of the source can be expressed by $1/S = a + b\lambda$, where $a = 1/\tau$ and $b = 1/C_2 \ln B$ where B is the fraction of the blackbody intensity for the temperature in question.* The pyrometer used in the present work on arc temperatures is provided with a red as well as a green screen, the "effective wave-length" of the red glass being determined. For the short focus lens combination sighted on a blackbody, no difference in match could be observed in changing over from red to green. The difference, however, with the front lens removed becomes appreciable.

If $\log D$ for the front lens component is the same for both wave-lengths (where D is the transmission factor), then

$$\log D = \frac{0.4343 C_2}{\lambda_g} \left(\frac{1}{s_1} - \frac{1}{s_2} \right) = \frac{0.4343 C_2}{\lambda_r} \left(\frac{1}{r_1} - \frac{1}{r_2} \right),$$

* Henning, 'Z. Electrochem.', vol. 30, p. 309 (1924).

and if ρS_1 is the same as ρS_1 , it follows since λ_r is different from λ_r , that ρS_2 cannot be the same as ρS_2 , and when sighted at long focus on a blackbody there will no longer be an intensity match, unless $D = 1$.

The differences observed will be different if the source does not radiate as a blackbody, and it becomes possible to obtain information about the selectivity of the source from such observations. If the source is a greybody, in the visible region of the spectrum, accurate observations of the brightness temperature in two wave-lengths will lead to a determination of the colour temperature of the source, which usually sets a high limit to the true temperature, as the brightness temperature sets a low limit. It is for these reasons useful to provide the pyrometer with at least two monochromatic filters.

The authors take the opportunity to thank Imperial Chemical Industries, Ltd., for grants in connection with research at high temperatures, and also Dr. Forsythe, of the General Electric Company, Cleveland, Ohio, for kindly providing two Tungsten strip lamps.

Summary.

1. The advantages of a magnifying pyrometer are pointed out.
 2. A monochromatic filter, using a "didymium glass," is described which transmits a band of light between 5740 and 5600 Å.
 3. The calibration of a pyrometer by simple methods is discussed, using a wedge as a blackbody source or a platinum tube provided with a small hole. The temperatures are determined by melting small pieces of metal on the outside of the tube or wedge, or preferably by hanging a wire down the middle of the tube.
 4. The advantage of the use of two monochromatic filters is pointed out, so that the colour temperature can be determined.
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An Integrating Photometer for X-Ray Crystal Analysis.

By B. WHEELER ROBINSON, M.A., The Royal Institution.

(Communicated by Sir William Bragg, F.R.S.—Received October 11, 1930.)

[PLATE 2.]

The measurement of the relative intensities of reflection of X-rays from lattice planes of a crystal is of vital importance in modern structure analysis, but it presents a problem often difficult of solution. The use of the ionisation spectrometer is laborious and sometimes impossible, at any rate for the small crystals which may be the only ones available; while photographic methods cannot usually be applied to records in which the distribution of energy over area varies considerably from one spot to another.

A new principle of photographic photometry was suggested by Astbury* to overcome the difficulty and to make it possible to obtain, as a single observation, a measure of the integrated energy corresponding to a narrow beam of radiation, not necessarily of uniform distribution, falling on a photographic plate. Briefly the method involves the reproduction of the photograph by the bichromated gelatin process as a thin membrane whose thickness diminishes with increasing opacity of the original; this membrane is then used as an obstacle to a beam of α -particles from a uniform polonium source, and the ionisation produced by the α -particles penetrating the tissue is found to measure the energy which formed the spot on the original record.

Astbury in the papers referred to has described a simple α -ray photometer constructed on these lines, and has shown how it may be used for intensity measurements. The present paper aims at giving an account of an improved instrument as it is now in actual use at the Davy Faraday Laboratory of the Royal Institution, London. It will be divided into the following sections:—

- (a) Discussion of the new instrument.
- (b) Technique of intensity measurement by this method.
- (c) Review of results obtainable.
- (d) Conclusion.

Section (a).—Discussion of the New Instrument.

The essential parts are shown in fig. 1, which is diagrammatic only. The gelatin tissue print is held taut between two mica sheets M_1 , M_2 , in which are

* 'Proc. Roy. Soc.,' A, vol. 115, p. 640 (1927), and vol. 123, p. 575 (1929).

apertures O_1 , O_2 ; O_2 being slightly smaller than O_1 and serving to define the maximum aperture of the instrument. A surface S , uniformly coated with

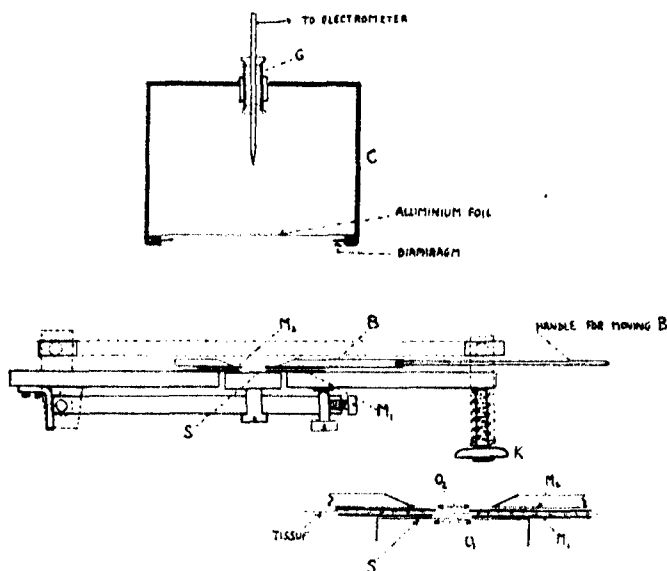


FIG. 1.

polonium, is parallel to M_1 and as close to it as possible; ideally it should be in actual contact with the tissue being measured. It is carried on point bearings and can be drawn aside and then replaced in the same position; when it is aside, the tissue can be inspected through the mica M_1 with the aid of oblique illumination from an electric lamp.

Above M_2 and very close to it is a brass slider B moving between stops and carrying holders for other diaphragms if necessary, which can thus be easily interchanged in front of the tissue. M_2 and the slider are carried on a brass frame which is hinged along one side and suitably mounted on springs, so that pressure on a knob K releases the tissue normally held between M_1 and M_2 and enables it to be adjusted in position with respect to the aperture system.

The ionisation produced by the α -particles penetrating the tissue is measured in the cylindrical chamber C , faced with thin aluminium leaf, and running on geometric rails so that its distance from tissue and source can be varied, recorded and reproduced. An electrode carried on an insulating plug and surrounded by an earthed guard ring G is connected to a Dolezalek electrometer; the body of the chamber is maintained at a negative potential of some 300 volts. A variable condenser in parallel with the insulated electrode enables

the sensitivity to be easily adjusted. All insulation is of amber, and the whole system is enclosed in an earthed case. With the electrometer (which was specially fitted with a very light needle, giving good damping and short period) at a sensitivity of about 300 divisions per volt, no trouble has ever been experienced with electrical leaks or unsteadiness.

For measuring the ionisation current various systems of "constant deflection" have been tried, but so far none has been found to equal, for speed and convenience, a simple determination of the rate of charging up of the electrometer system. The vertical filament of an automobile headlamp bulb is sharply focussed by way of the electrometer mirror on to a horizontal slit, behind which is a sheet of bromide paper moving in vertical guides. A shutter, electrically controlled from a swinging pendulum, makes exposure only on the intervals 0 1 2, 10 11 12, 20 21 22, etc., either through an automatic counter switch or separately under the control of the experimenter. Many records may be made in succession on the sensitive paper; after development the distances 0-20, 1-21, etc., are quickly measured and averaged out, giving a result for the speed of travel of the spot which exceeds in accuracy the more usual and less convenient stop-watch determination.

In order to secure uniformity of the source over the aperture, Astbury was compelled to rotate it continuously during the measurement of ionisation. By the following technique it has been found possible to produce a source having the requisite (1 per cent.) uniformity over a surface some 3 mm. square. An extract of old radon tubes was made in dilute (N/10) nitric acid. A polished silver disc was cleaned as carefully as possible, and then lightly sputtered with platinum by a vacuum discharge. Radium F was then immediately deposited on the sputtered surface by electrolysis from the acid solution with a current not exceeding 5 microamps. per square centimetre for a period of some hours, the electrode being continuously rotated during this time.* After washing with distilled water and drying the uniformity of the surface was checked by exploration with a gold leaf electroscope and a pin-hole diaphragm adjusted to be parallel and very close to the radioactive surface and traversed by a graduated mechanical micrometer stage. Using a screen of thin aluminium foil a test was also made for β -radiation, due to the presence of radium E, which would undesirably affect the working of the photometer. A satisfactory source made in this manner may be mounted in position and not again disturbed during its useful life, which of course will depend on its initial intensity (half period of polonium, 140 days).

* Curie, 'J. Chem. Phys.', vol. 22, p. 471 (1925).

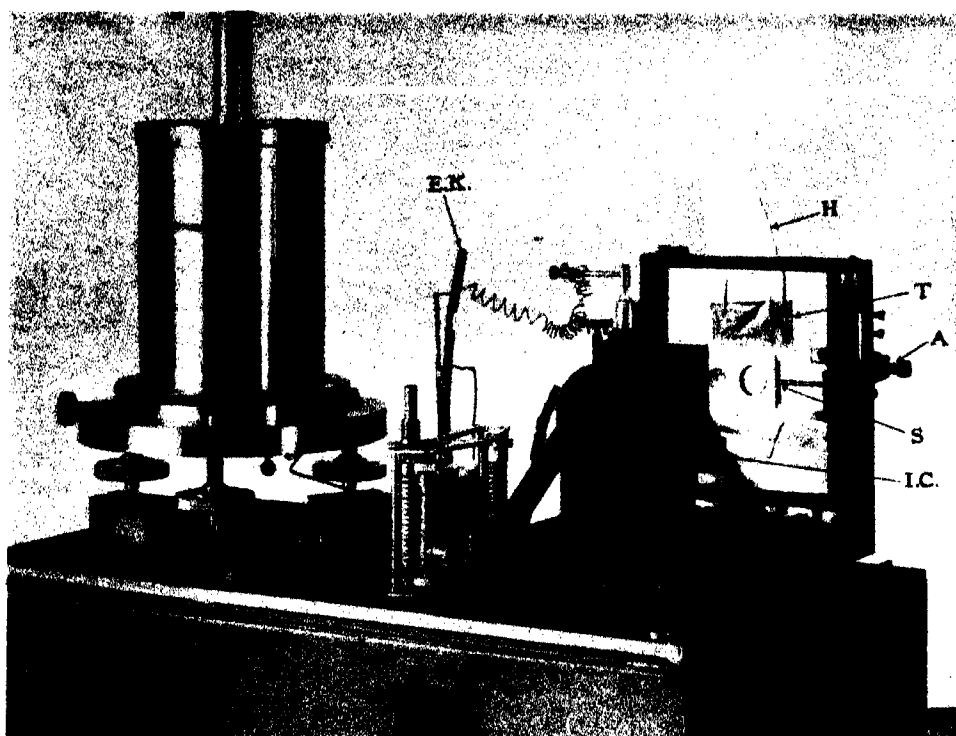


FIG. 2.—E.K., Earthing key. H., Handle. T., Tissue. A., Arm carrying source. S., Slider. I.C., Ionization chamber.

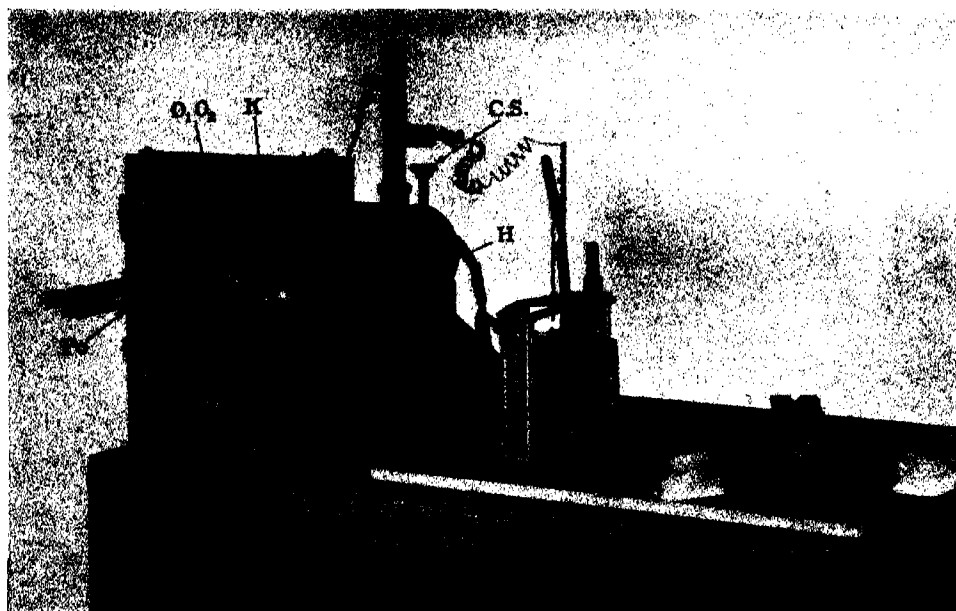


FIG. 3.—Po., Polonium surface. O.O., Apertures. K., Release knob. C.S., Clamping screw for chamber. H., Handle for moving slider.

(Facing p. 123.)

Figs. 2 and 3 (Plate 2) show the instrument in greater detail. Improvement may be claimed over the original model in the following ways : (a) the power of adjustment of the tissue *in situ*, without the removal of the whole of the aperture-carrying frame from the apparatus ; (b) the greater convenience of the method of current measuring adopted ; (c) the power of exchanging one aperture for another and of moving the ionisation chamber easily with reference to the source, both of which adjustments are essential, as we shall see, to the practical use of the instrument.

The integrating properties of the photometer have been discussed by Astbury (*loc. cit.*). Briefly the matter may be put as follows :—

The curve usually connecting the X-ray energy incident on a photographic plate and the optical density produced is of a logarithmic type,* and in consequence no simple treatment of the density produced by a given bundle of radiation can be made to give a direct measure of its total amount. The advantage of using the seemingly indirect gelatin process is that this curve is compensated for by the (α -ray ionisation)—(tissue thickness) relation, and that in consequence it is possible to obtain a *linear* relation between original X-ray energy at a point and final ionisation current arising from that point. It may here be emphasised that this linearity is by good fortune rather than by design. Once this linear relation is obtained, the integrating property follows directly, as we can see by regarding the spot on the tissue as an assemblage of small areas side by side, each uniform in thickness and each making a contribution to the total ionisation current strictly proportional to the X-ray energy which fell on that area in the original photograph. Consequently the first step in any measurement is to ensure that this linear relation holds for the particular photograph and tissue concerned. This is done by imprinting on each photograph before development a set of " calibration spots " of known energy ratios ; the method of doing this with a rotating sector has been described by Astbury. These spots, representing uniform patches of radiation of known relative energies, are measured on the photometer, which is adjusted until a linear energy-ionisation relation is secured.

There are several practical considerations which may serve to limit the accuracy of the instrument when used in this way as an integrating photometer. In the first place, we have considered above that the tissue is in effect infinitely thin, and that it is backed by an infinite uniform radioactive source. Actually the tissue has a maximum thickness of about 1/50 mm. ; more serious than this, it is held between mica diaphragms of much greater thickness, and the

* Bouwers, 'Z. Physik,' vol. 14, p. 374 (1923).

source cannot be in contact even with these. Altogether in the present instrument a distance of about $\frac{1}{2}$ mm. occurs between the face of the source and the distant surface of the smallest diaphragm mounted on the slider, as compared with an aperture of 3 mm. and a chamber distance of perhaps 15 mm. No errors have yet been traced to this cause, and we should not expect them, for as long as the uniform surface of the source completely fills the aperture of the instrument (as defined by the diaphragm on the ionisation chamber and the smallest of the diaphragms near the tissue) the theoretical conditions are satisfied to a sufficient degree of approximation. As Astbury has pointed out, errors will not arise from the varying thickness of tissue until the tangent to the tissue surface at any point lies within the widest possible cone of α -rays passing through that point.

It is also interesting to enquire to what degree departures from the exact linearity relation may be permitted in the adjustment of the apparatus. To check this, a likely "density profile" of a series of spots was assumed, and the total energy worked out by arithmetical integration (a) assuming the instrument to be correctly adjusted to a linear energy-current relation, and (b) with two arbitrary relations obtained during the course of adjustment (fig. 4). Of

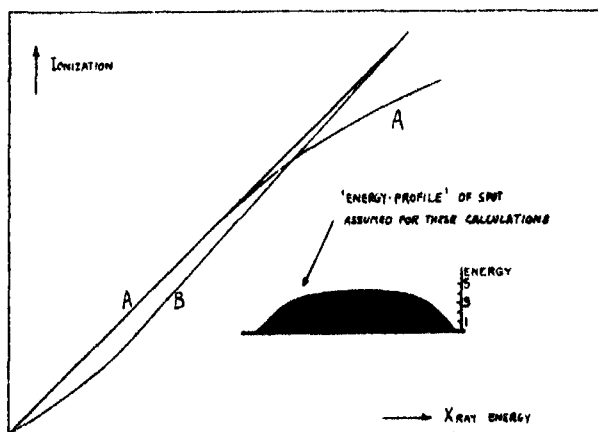


FIG. 4.

these, B represents the effect of having the ionisation chamber too far from the source, while A is due to insufficient contrast in the original negative, or, of course, to excessive exposure of the calibration spots. For purposes of calculation it was assumed that the spots had central symmetry. The following table shows the results obtained.

Table I.

True energy values of the spots	100	60	30	10
Calculated value, curve A	87.3	60	30.9	10.0
Calculated value, curve B	109	60	25.1	7.6

It will be seen that serious errors must be expected unless careful adjustment of the apparatus is made. For this purpose it would be an advantage to record on the photograph a more numerous series of spots than has up to the present been done (six spots, energy ratios 1 : 2 : 4 : 6 : 8 : 10). In favourable conditions energy-current relations are obtained so nearly linear (cf. curve C, fig. 5) that no measurable differences from the theoretical values would be expected from this cause.

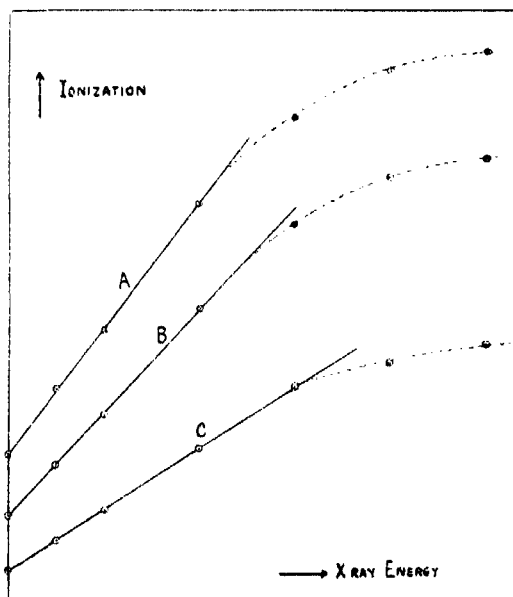


FIG. 5.

A rough calculation gives 500 as the number of α -particles which reach the ionisation chamber per second when a strong spot is being measured. This number could, of course, be increased by obtaining a stronger radioactive source ; but it means that at present, in order to secure a 1 per cent. accuracy in the measurement of the ionisation current, 20 seconds at least—or 10,000 particles—must be occupied in this measurement. It is largely for this reason that a “constant deflection” method of measurement, which might have had

advantages with β -ray ionisation for example, was not adopted in the present arrangement.

Section (b).—The Technique of Tissue Measurement.

To secure the most accurate results of which the photometer is capable, the following precautions must be observed :—

(a) The full extent of the linear portion of the intensity-ionisation graph must be employed. That is to say, the exposure of the photograph must be so regulated that the densest portion equals but does not exceed in density the densest calibration spot whose value lies on the linear portion of the graph. Also the instrument must be so adjusted for each tissue as to make this portion as long as possible, and to secure the maximum value of the ratio i/i_0 where i is the ionisation current corresponding to the extreme linear point on the curve, and i_0 is the current corresponding to the background portions of the tissue. This ratio represents the degree of contrast permissible between spot and background, and may vary as much as from 2 to 5 with instrumental adjustment in extreme cases. Thus fig. 3 shows how this ratio was found to vary with chamber position in one experiment.

(b) The aperture employed must closely circumscribe the spot; this is essential for accuracy, as otherwise the effective value of the contrast of spot to background may be seriously diminished. Before measurement the tissue must be carefully examined and an aperture chosen which conforms to the general shape of the spots and is able to contain the largest.

Apart from the actual preparation of the tissues, which is fully described by Astbury (*loc. cit.*), and which involves no labours greater than those required for any careful photographic work, the chief difficulties of measurement with the integrating photometer are in—

- (a) Identifying the spot on the tissue and correctly bringing it before the aperture of the instrument.
- (b) Correctly estimating the background value which is to be deducted from the values of ionisation observed for each spot.

In regard to (a), all but the strongest spots are invisible when once the tissue is inserted in the instrument, so that some form of marking them is essential. Laying the tissue on a well-illuminated opal screen, the spots mostly become visible, and their positions can be handily marked by the use of a special device—a glass plate illuminated from beneath, on which are marked two cross lines and above which a swinging arm, mounted on bearings, carries an inked rubber

stamp which will imprint on the tissue a narrow ring of which the cross lines are diameters. Each spot in turn is brought to the cross lines and thus encircled; the rings are slightly larger than the maximum aperture of the instrument, are easily visible when the tissue is in position, and give a ready means of centring each spot on the aperture system. The most feeble spots are not visible, however good the illumination of the tissue; their positions may be marked with the same device by laying the original negative under the tissue, when their location becomes apparent, using the stronger spots as reference points.

(b) The background estimation sets the limit in practice to the accuracy of the instrument. The following figures show the extent to which background variation occurs, apart from any X-radiation incident on the photograph. They were obtained by developing an unexposed film in the usual way, and exposing a tissue underneath it; they represent the values of ionisation current (in arbitrary units) obtained at 12 points regularly spaced over the extent of the tissue, which measured roughly 3 by 4 inches.

Table II.—Variation of Background.

11.60	11.54	11.05	11.56
11.18	11.55	11.67	11.80
11.32	10.86	11.29	11.61

Average value of deviation from mean is about 2 per cent.

When we consider that the value of the current on the same scale corresponding to an intense X-ray spot, of moderate size, would be 20 units, we see that there is here a serious limitation to the accuracy of any such photographic method. In actual practice, of course, superposed on these background fluctuations are the additional variations of general X-ray scattering, also the medley of continuous spectra corresponding to each crystal reflection, since a highly monochromatic source is not in general employed in crystal photographs. On the other hand, we must remember that these fluctuations are not systematic, and that in consequence their effects can be eliminated by taking a sufficiently large number of separate observations. This is in fact what has been done in some of the figures quoted in the next section.

Three methods of dealing with the background have been used hitherto in the measurement of photographs:—(1) Where the spots are large or the background variations are small, an observation of the background is made in between each spot and the next, and the average of the background values

bracketting each spot is taken as the true value for the spot. (2) When special accuracy is desired, as for example in the comparison of two feeble spots, a whole ring of background values may be noted circumscribing each spot, and the average of all taken. (3) As the most satisfactory method for ordinary crystal photographs where the spots are small, two complementary diaphragms are used; one has a central aperture shaped to the general outline of the spots, but in the other the centre is blocked out by a suitable obstacle opaque to α -rays (such as a thin piece of metal foil) cut to this outline and carried in the centre of the opening by fine glass fibres to which it is cemented. The tissue having been adjusted in position, a reading is taken with each of these diaphragms; the second one will give an estimate of the background intensity all round the area measured by the first, and its value, multiplied by a constant factor depending on the ratio of the two areas concerned (which may quickly be determined from a measurement on a blank portion of the tissue) is to be subtracted from the first to give the correct intensity value of the spot.

The best way of manœuvring the tissue seems to be to cut it into portions not more than $1\frac{1}{2}$ inches wide and to affix to each portion a "handle" of thin stiff paper, at two or three points only to avoid crumpling, with a very small amount of seccotine. The handle projects above the frame of the photometer (such a mounted tissue can be seen in Plate 2) and enables it to be readily moved about.

The various steps in the measurement of a tissue in the photometer are then as follows:—(1) The spots are ringed, and numbered for reference with a soft lead pencil, which fortunately will write easily on the matt side of the tissue; the tissue is divided into convenient portions and handles are attached. It is always worth while at this stage to make an exact tracing of the positions and general appearance of the spots on the photograph, on which the identification numbers may also be recorded. (2) The portion of tissue containing the calibration spots is inserted in the instrument and the position of the ionisation chamber is found at which α -ray current from a background portion of tissue is just detectable; the chamber is moved $3\frac{1}{2}$ mm. nearer (this position is found on the average to give the best results) and is clamped there. Then the calibration spots are measured, the sensitivity being adjusted to give a convenient maximum value, and the readings are plotted against the known energy values. If additional adjustments of diaphragm or chamber distance are necessary to improve the linear relation, they are made; but in the majority of cases no alteration is necessary if standard conditions of development and printing have been maintained. (3) The photographic recording mechanism is started and

the measurements of the spots carried through, being usually repeated twice in succession. (4) The paper record is developed, fixed and dried, its readings measured and tabulated, and the final energies deduced. (5) Any discordant values are repeated if necessary.

As a rough estimate of the labour involved in these processes, the following figures may be taken as typical, assuming that there are no delays or mishaps. Twelve quarter-plate tissues will take an hour to sensitise and 3 hours to print (these times could be much diminished by larger-scale apparatus and organisation). To measure each tissue, supposed to be showing, perhaps, 35 measurable spots, will require $\frac{1}{2}$ hour to mark and number, $\frac{1}{2}$ hour to adjust the photometer, $1\frac{1}{2}$ hours to measure, $\frac{1}{2}$ hour to work out figures; repetition and corrections, 3 hours, or 6 hours in all (excluding the time taken in tissue preparation, a task which could well be delegated to a careful assistant) for the 35 measured intensities.

Section (c).—Review of Results Obtainable.

The significance of the readings obtained from an instrument of this kind may be queried in three stages; (1) Are measurements on the same tissue repeatable? (2) Does a redetermination of the same phenomenon give the same result? (3) Do the results agree with the same intensities as measured by the ionisation spectrometer?

As to (1) it may be said that on the average a repetition of figures to rather better than 1 per cent. of the strongest spots can be obtained, depending largely on the care which has been expended on making perfect tissue prints and in adjusting the size of spots to fill the maximum aperture of the instrument. The following table shows the accuracy attainable in successive measurements of the same value; four areas of tissue were each measured four times (the figures give the ionisation current in arbitrary units).

Table III.—Repetition of Results.

	Area A.	Area B.	Area C.	Area D.
	11·97	12·63	12·62	12·71
	11·91	12·60	12·57	12·71
	12·07	12·60	12·49	12·71
	12·07	12·67	12·67	12·82
Mean values	12·01	12·59	12·58	12·74

Average departure from mean, 0·06, or $\frac{1}{2}$ per cent.
Maximum departure from mean, 0·12, or $\frac{1}{4}$ per cent.

The measurement of spot intensities, regarded as the difference between two readings (the total ionisation and the background value) will not of course be as good as this in general. The following is a typical example of two sets of measurements (A) and (B) of the same tissue.

Table IV.—Remeasurement of same Tissue.

Intensity.	Spot number.								
	1	2	2	4	5	6	7	8	9
(A)	4.3	5.3	1.0	2.2	4.7	6.4	101.7	50.8	5.0
(B)	5.0	7.6	3.1	4.3	5.7	8.0	103.0	47.9	4.5

Intensity.	Spot number.								
	10	11	12	13	14	15	16	17	18
(A)	6.2	6.8	9.1	4.2	4.5	7.2	8.2	8.2	4.7
(B)	4.7	6.7	8.8	3.4	3.3	5.3	6.7	7.4	5.3

Intensity.	Spot number.							
	19	20	21	22	23	24	25	
(A)	34.9	59.4	4.0	54.5	8.0	7.4	3.0	
(B)	36.0	60.5	5.0	53.0	7.1	7.4	5.0	

Average difference between series (A) and (B) is 1.2 per cent. of the largest spot ; maximum difference is 2.9 per cent.

One day elapsed between these two sets of readings, and different diaphragms were used in the background estimation for the two sets.

As an example of the consistency attainable between successive measurements of the same phenomenon, the following figures may be quoted, from data obtained in a special comparison of the intensities of reflection of copper $K\alpha$ -radiation from the (110) and (320) also the (200) and (410) planes of an anthracene crystal. Oscillation photographs were taken giving these pairs of reflections on the same film, three exposures of the first and two of the second pair being made. The significant portions of the films with their appropriate calibration spots were cut out and mounted into one composite negative,

from which three separate tissue prints were made. The following results were obtained.

Table V.—Comparison of Intensities (Anthracene 320/110 and 410/200).

	Tissue 1.	Tissue 2.	Tissue 3.	
Plate 1	5.7	6.6	7.8	} *Intensity of (320) [relative to (110) taken as 100].
Plate 2	6.3	6.4	8.7	
Plate 3	6.5	7.3	9.2	
Plate 4	4.5	5.1	6.9	} *Intensity of (410) [relative to (200) taken as 100].
Plate 5	4.7	5.2	6.9	

* N.B.—These values refer to the apparent intensity as recorded on the plate; they are still subject to a correction for oblique incidence (*cf.* Cox and Shaw, 'Proc. Roy. Soc.,' A, vol. 127, p. 71 (1930)).

It was found impossible (probably owing to over-exposure of the tissue) to obtain a satisfactory linear relation with the tissue 3; this is reflected in the consistently higher values which it shows. Nos. (1) and (2) were satisfactory in this respect, and it will be seen that the agreement between what are in effect six independent values of the intensity ratio 320/110 is very good.

Finally we may enquire how far the results obtained by the photographic method agree with those carried out by the more usual ionisation methods. A set of measures has been made on the equatorial planes of the *c* zone of anthracene. In order to give a photograph in which the spots were distributed with reasonable uniformity over the area of the film, and in which there should be a minimum of fogging, a simple "rotating film" camera was built for this purpose. A film in its paper envelope is bent round the circumference of a wooden cylinder (which it exactly occupies), which rotates on a horizontal axis in step with the anthracene crystal on its vertical axis, the two being connected by chain and sprocket gearing. A horizontal slit allows only the equatorial reflections to reach the film. Such a camera is easy to construct, and gives clean photographs free from fogging, eminently suitable for intensity measurements; it also shows up defective crystals, and makes very easy the identification of the indices of the spots, since one co-ordinate of the film represents the angular position of the crystal at the moment of reflection.

Four such photographs, using three different crystals, of the equatorial planes of the *c* zone of anthracene were made; the table shows the average of these results, corrected for oblique incidence from the figures of Cox and Shaw (*loc. cit.*), and compared with the corresponding intensities measured by

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the ionisation method, for which I am greatly indebted to Sir William Bragg.

Table VI.—Comparison of Photographic and Ionisation Methods.

Intensities of reflection in *c* zone from anthracene (copper K α) (*hk*0 and *h* $\bar{k}$ 0 averaged together).

Index of plane.	Intensity. (photographic, B.W.R.).	Intensity. (ionisation, W.H.B.).
020	11.2	11.8
200	100.7	100
110	99.5	100
120	3.7	—
130	2.4	4.4
210	52.1	52.0
220	1.5	5.0
310	1.1	1.7
320	7.2	7.4
410	5.5	5.6

This agreement seems better than we should expect from a process involving so many separate stages, each with its own possibilities of error. We must remember, however, that the figures in the column above represent the average of many measurements, with different crystals, films, tissues and calibrations, so that non-systematic errors will have been largely eliminated. The figures certainly encourage the belief that the photographic method, as far as accuracy is concerned, is as reliable as the other.

Section (d).—Conclusion.

The weaknesses of the x-ray photometer are clear enough ; in particular the additional photographic process introduces irritating complication, care must be taken that the photographs (as regards size of spot, exposure, and background clearness) are really suitable for such photometry, and it is not possible to repeat isolated readings without a disproportionate amount of labour. But the results quoted here would at least seem to show that the photometer has an undoubted position in the technique of X-ray intensity measurement as it stands to-day. For work on the structure of spectral lines and the like, a line microphotometer of the Moll or Cambridge type would be preferred, and for the measurement of individual intensities the ionisation spectrometer, if sufficiently sensitive, has the advantage. But for the complete survey of the intensities of reflection from a crystal, particularly when the crystal is small or easily volatile and a photographic method must be used, the α -ray

photometer is the best, perhaps the only, instrument to employ. It is elegant in conception, and no doubt some of the present difficulties of execution will be removed by further experience. A survey of the intensities of reflection of an anthracene crystal, rotated about an axis perpendicular to the (001) planes, in which over 200 separate reflections have been measured, has just been completed by this method in this laboratory.

My thanks are due to Sir William Bragg and the Managers of the Royal Institution for the opportunity of carrying out this work, to various fellow-members of this laboratory for helpful suggestions and discussions, and to Mr. C. H. Jenkinson for the great skill with which he has carried out the construction of the apparatus.

Investigations in the Infra-Red Region of the Spectrum.
Part I.—Introductory and Experimental.

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London.

(Communicated by F. G. Donnan, F.R.S.—Received August 11, 1930.)

[PLATE 3.]

Robertson and Fox in their fundamental memoir* have published a comprehensive account of the precautions necessary for obtaining reliable results with a prism spectrometer in the infra-red between 1 and 17 μ . The authors feel, however, that some advantage to other workers may accrue if they in turn outline their own particular difficulties with the manner of their resolution. It may be stated at once that it is now possible to make scale readings to an accuracy of 1 mm. *during the day*, with a galvanometer sensitivity of 10^{-10} to 10^{-11} amp. per millimetre deflection at 1 metre distance. If it is realised that the work is carried out on the top floor of the Chemistry Department of this Institution, in a building which houses some dozen electrical generators and a large liquid air plant, with a stream of heavy bus traffic 10 yards from the building and a tube railway at 100 yards, it will be seen that the usual experimental difficulties have been completely overcome.

* 'Proc. Roy. Soc.,' A, vol. 120, p. 128 (1928).

Preliminary experiments were made in a constant temperature room in the basement; the humidity was high and had a deleterious effect on the rocksalt portions of the apparatus, whilst the discomfort of night work in such a room was extreme. It was consequently decided to re-approach the problem from the beginning, but not before trials had shown that where the motion of the building as a whole is small, comparatively simple expedients serve to eliminate most of the mechanical disturbance. This was cut out by placing the galvanometer with its Paschen shields (total weight about 250 lb.) on a large block of wood supported by four pairs of inverted small porcelain crucibles placed at the corners. Eight of the thinnest available crucibles were selected; the two in a pair were placed one on top of the other and separated by a small piece of 5-ply wood and a few pieces of filter paper. If the galvanometer and shields are not too heavy, the replacement of the rubber shock absorber in the ordinary anti-vibration spider by a crucible and one or two layers of filter paper was found very efficient.

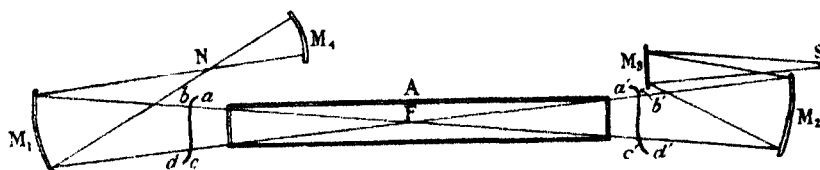
General Lay-out.

The room is supplied with electric power at a constant voltage of 250 from a battery of accumulators. The advantage of the assemblage chosen (discussed in detail below) is that all controls can be easily manipulated by one person without moving from his seat. The spectrometer was a Hilger D.42 constant deviation instrument, fitted with quartz, fluorite, rocksalt, and sylvine prisms. The light from a Nernst filament, N (see figure), contained in an asbestos housing, passes through the absorption tube, A, and is brought to a focus at the spectrometer slit, S, by means of a mirror, M₂. The thermopile is coupled to a sensitive Downing galvanometer carried on a modified Julius suspension. A mercury vapour lamp encased in an asbestos box is used in setting the Wadsworth mirror. The wave-length drum of the spectrometer is propelled by contact with a rubber-covered, low-g geared wheel capable of rotation from a distance.

Source of Radiation.—Nernst filaments were procured from the Glasco Lampen Gesellschaft, M.B.H., Lausitzer Platz 4, Berlin, S.O.36; their life is considerably greater than the home product. An asbestos housing encloses the filament and is fitted with an aluminium shutter running in brass guides; this housing is so constructed that a constant air current flows past the filament which is operated at about 0.8 amp. and 90 volts from the constant voltage supply. Absolute constancy of filament current is maintained by the potentiometer device described by Robertson and Fox (*loc. cit.*). Fractures may occur in the filament and are repaired by cementing the break with a mixture of zir-

conium, cerium, thorium and yttrium oxides and a trace of borax, the whole made into a paste by the addition of a 12 per cent. solution of cane sugar.*

Focusing the Radiation on the Collimator Slit—Radiation from the condensing mirror, M_1 , is focused at the centre, F , of the absorption tube,† and then diverges to M_2 which focuses it, after reflection at a plane mirror, M_3 , on the collimator slit, S . A good image of the filament is obtained on S only if the errors introduced by M_1 are reversed by M_2 .‡ A wave diverging from the Nernst filament, N , towards M_1 is after reflection distorted to some form $abcd$. When it has passed through F , its form will be $a'b'c'd'$, and this wave should



be brought to a focus as nearly perfect as possible by M_2 . If $abcd$ were travelling from right to left instead of from left to right, M_1 would bring it to a correct focus at N . Hence the point to which the radiation converges should lie on that side of the direction of the oncoming wave which is turned away from the mirror; that is, the focus conjugate to F in the mirror M_2 should lie on the a' side of M_2 . The focal length of M_2 should be such that the angular aperture of the spectrometer is just filled, and that of M_1 such that the image of the Nernst filament is just the length of the collimator slit. M_4 is a reflecting mirror which increases the effective solid angle subtended by M_1 at N .

Thermopile and Galvanometer.—After traversing the spectrometer, the radiation passes through the spectrometer slit on to a 20 junction bismuth-silver thermopile enclosed in an air-tight case,§ which may be evacuated; the Hilger thermopiles are constructed for maximum efficiency at atmospheric pressure in air, but it was found advantageous to maintain a slightly diminished pressure in the case. The galvanometer was of the Downing type|| and was employed normally at a sensitivity of $10^{-10.5}$ amp. per millimetre scale deflection at 1 metre; it was possible to obtain values of 10^{-11} , but the period became unduly long with the instrument employed; another of the same type has been procured with a lighter system to overcome this difficulty. Electro-

* Griffiths, 'Phil. Mag.' [vi], vol. 50, p. 263 (1925).

† Snow and Taylor, 'Proc. Roy. Soc.,' A, vol. 124, p. 445 (1929).

‡ Cf. Czerny, 'Z. Physik,' vol. 61, p. 792 (1930).

§ Robertson and Fox, *loc. cit.*

|| 'J. Sci. Inst.,' vol. 3, p. 331 (1926).

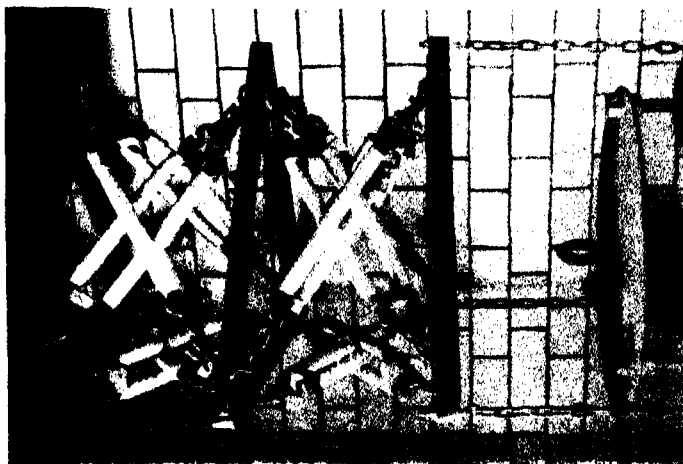
magnetic disturbances were suppressed by surrounding the galvanometer with a loosely wound copper and mu-metal shield; over this were placed the two Paschen shields between which mu-metal was again loosely wound. The mass of the shields with base plates, etc., was determined and the centre of mass located. A modified Julius suspension was then constructed based very largely on the design of Johnsrud;* it is illustrated in Plate 3. The tape-bound springs act as shock absorbers, and the adjustable cylindrical masses allow the centre of mass to be brought to the point of suspension of the magnet system. With all leads from thermopile to galvanometer enclosed in earthed composition tubing, the necessity for night work has been completely overcome. The relatively large mass of the whole makes shielding against draughts unnecessary.

Absorption Tubes.—These were 45 cm. long by 4.5 cm. diameter, of glass, with the ends ground parallel and polished; the circular rocksalt plates were pressed against the ends with a trace of vaseline; the tubes were then evacuated, and if leaks appeared shellac varnish was wiped over the join. The end caps and rings and the rocker are fully described by Robertson and Fox (*loc. cit.*); the latter was operated from a distance and allowed of adjustments for parallelism and height, since the centres of the tubes must be at the same level as the centres of the Nernst filament and spectrometer slit for efficient working. The gas enters the absorption tube through a large glass spiral as described in the paper cited, thus allowing for the ready interchange of the evacuated control tube with that containing the gas; the spiral is connected through phosphoric oxide tubes and a liquid air trap to a Hyvac pump and manometer.

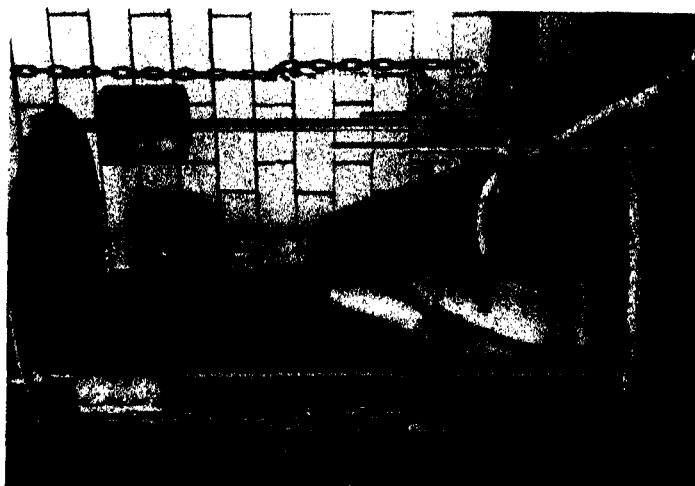
The Spectrometer.—The spectrometer is a Hilger D.42 instrument; it was encased in 5-ply wood painted dead black inside. The only parts which project are the wave-length drum, the collimator slit, and the thermopile eyepiece cover; care was taken to ensure close fitting around these parts. The case was bored to take a thermometer and a tube for the evacuation of the brass, airtight thermopile case. The temperature of the case was maintained reasonably constant at 18°; all results, however, are ultimately corrected for that temperature. A small quantity of desiccating agent was kept inside the case.

Quartz, fluorite, rocksalt and sylvine prisms, each of 45 mm. height and 70 mm. length of face, with prism angle 60°, were available. One drum was used for all four prisms and was calibrated by Robertson and Fox's method. We should like at this point to express our gratitude to Sir Robert Robertson

* 'J. Opt. Soc. Amer.', vol. 10, p. 809 (1925).



Shock Absorbers.



Shielding system.

and his co-workers for their very ready help and guidance, and for the loan of an accurate steel tape measure and a telescope fitted with a high power eyepiece used in the calibration of the instrument.

Possibilities of Experimental Error.—Apart from the lengthy and laborious process of drum calibration, investigation into a number of other possible errors in the setting of the instrument is necessary before the potentialities of this type of spectrometer can be thoroughly exploited. The absence of any such data was found a great handicap at the beginning, and the valuable work of Robertson and Fox admits of supplement. It is proposed in what follows to discuss very briefly the sources of possible errors and to indicate their calculation.

The possible experimental errors are due to uncertainty in—

- (i) drum reading ;
- (ii) setting the prism at minimum deviation ;
- (iii) value of the prism angle ;
- (iv) temperature of the prism.

They are best calculated in terms of error in the rotation of the prism table.

(i) *Errors in Drum Reading.*—The error in the drum calibration itself is easily calculated and gives an error in rotation of the prism table less than 3 seconds of arc for any rotation of the drum.

(ii) *Errors in Setting the Prism at Minimum Deviation.*—Messrs. Hilger have shown in the tables of accompanying data supplied with the instrument that an error of 30 minutes in the minimum deviation setting corresponds to a maximum possible error of 7 seconds in the rotation of the prism table. The process depends finally on the setting of the prism by the aid of a jig in which the possible error is approximately 5 minutes ; hence the possible equivalent error in prism table rotation is 1.5 seconds.

(iii) *Value of the Prism Angle.*—A knowledge of the accuracy required for the prism angle is of great use, particularly for the rocksalt and sylvine prisms ; the faces of the latter may deteriorate and require repolishing. The refracting angle may be changed in the process ; if the change is not sufficient to give an equivalent error in prism table rotation greater than 1 second, the wave-length drum need not be recalibrated. The minimum deviation, δ , for any refractive index, n , and prism angle, A , is given by

$$n = \sin \frac{1}{2} (A + \delta) / \sin \frac{1}{2} A. \quad (1)$$

Hence

$$\frac{\partial n}{\partial A} = 0.243 \frac{\sin \frac{1}{2} \delta}{\sin^2 \frac{1}{2} A},$$

where ∂n is the change in the fifth decimal place of refractive index per second of arc change in A ; if $A = 60^\circ$,

$$\frac{\partial n}{\partial A} = 0.971 \sin \frac{1}{2} \delta. \quad (2)$$

The equivalent change in total deviation is obtained by multiplying (2) by $(\partial \delta / \partial n)$; from (1) we have

$$\left(\frac{\partial \delta}{\partial n} \right) = \frac{2 \sin \frac{1}{2} A}{\cos \frac{1}{2} (A + \delta)}. \quad (3)$$

Inserting appropriate values for rocksalt in (3), we obtain a change in total deviation per unit change in the fifth decimal place of refractive index of 3 seconds; this is approximately constant throughout the range of 1 to 16 μ , since $\frac{1}{2} (A + \delta)$ is large compared with the difference in the values of $\frac{1}{2} \delta$ at 1 μ and at 16 μ . Combining this with (2) we have

$$\left(\frac{\partial \delta}{\partial A} \right)_{1\mu} = 1.0 \text{ second/second.}$$

$$\left(\frac{\partial \delta}{\partial A} \right)_{16\mu} = 0.8 \text{ second/second.}$$

Hence the equivalent error in prism table rotation for an error of 1 second in A is 0.5 second at 1 μ and 0.4 second at 16 μ ; the Wadsworth mirror is adjusted to give a correct setting at 1.014 μ , and the nett error at 16 μ is consequently 0.1 second. The permissible error in A is therefore 10 seconds of arc.

Similar calculations give the corresponding values for the other prism materials and they are tabulated below.

Table I.—Permissible Errors in Prism Angles at the Appropriate Wave-lengths.

Material.	$(\partial \delta / \partial n)$ in seconds.	$(\partial \delta / \partial A)$ in seconds/second.		Permissible error in A in seconds.
	(At 5th decimal place for n .)	At 1 μ .	At effective limit.	
Quartz, $60^\circ 1' 30''$	3.0	1.0	0.9 at 3.4 μ	20
Fluorite, $60^\circ 0' 0''$	2.9	0.78	0.61 at 8.5 μ	12
Rocksalt, $60^\circ 0' 0''$...	3.0	1.0	0.8 at 16 μ	10
Sylvine, $60^\circ 0' 37''$	2.9	0.89	0.63 at 22 μ	8

(iv) *Variation of Refractive Index of Prism Material with Temperature.*—The variation is considerable with rocksalt, fluorite and sylvine. The temperature at which the Wadsworth mirror is set, and that at which the spectrometer drum is read, are both noted ; the spectrometer is calibrated to read correctly at 18° C., and if the Wadsworth mirror is not set at 18° there is an equivalent error in prism table rotation. The article by Coblenz on “ *Infra-red Transmission and Refraction Data* ” in the “ *Dictionary of Applied Physics* ” (vol. 4, p. 136) records the necessary temperature coefficients which give the change in refractive index ; when the latter is multiplied by $\frac{1}{2}(\partial\delta/\partial n)$ we obtain the equivalent correction in prism table rotation ; a similar calculation provides the temperature correction for the drum reading, and the algebraic difference of the two gives the nett correction for $\frac{1}{2}\delta$; the corresponding error in wave-length is given on multiplication by $2(\partial\lambda/\partial\delta)$. The temperature at which the Wadsworth mirror is set, and that at which the drum is read, should be accurate to 0.3°.

The greatest error, then, is in the uncertainty of prism table rotation with drum rotation. The maximum possible error in any wave-length reading may be taken as that due to an error of 4 seconds of arc in the semi-minimum deviation ; this error diminishes as the wave-length approaches 1.014 μ , where the Wadsworth mirror is set.

Resolving Power.

A knowledge of the difference in wave-numbers of any two consecutive maxima which can be distinguished by the instrument is useful inasmuch as it indicates what Bjerrum doublets in the infra-red might be separated into their constituent branches. A thermopile slit width of 0.01 inch subtends an angle of approximately 100 seconds of arc at the prism ; if the collimator slit is of the same width, maxima separated by the wave-numbers included in 100 seconds of arc of total minimum deviation should be resolved ; since the direction of incidence on the prism is constant for all wave-lengths, spectral lines must on emergence be separated approximately as the difference in their total minimum deviations. The problem is therefore to determine the wave-numbers included in 100 seconds of arc of total deviation at different wave-lengths. The range of wave-length included in 100 seconds of arc is calculated from the table of wave-length—semi-minimum deviation. The range of wave-numbers is then determined from the expression $d\nu = -d\lambda/\lambda^2$.

Table II appended gives the wave-numbers included in the slit width used for normal working of the spectrometer within the appropriate ranges for the available prism materials.

Table II.

	λ (μ).	Normal slit width (in 1/1000 in.).	Wave-number separation (cm.^{-1}).
(a) Quartz	1.0	3	70
	1.5	3	50
	1.75	3	20
	2.0	3	13
	2.7	5	9
	3.0	7	8
	3.4	7	7
(b) Fluorite	3.5	5	19
	4.0	5	14
	4.5	5	10
	5.0	7	8
	5.7	7	7
	6.4	10	6
	7.2	10	4
	8.1	10	3
(c) Rocksalt	8.0	10	12
	9.3	10	8
	10.4	10	5
	11.6	10	4
	12.8	10	3
	14.0	15	3
	15.1	15	2
(d) Sylvine	15.5	15	4
	16.75	20	3.5
	17.9	20	3
	19.5	25	2.5
	21.5	25	2.5

The above wave-number separations are less, however, than those which in practice can actually be resolved, since curvature of the image of the collimator slit diminishes the resolving power. This defect might be considerably reduced if the spectroscope were designed so that the telescope mirror reversed the errors of the collimator mirror.* The P and R branches of the sulphur dioxide band at 4.003μ , separated by Meyer, Bronk and Levin† with the aid of a grating instrument, show a difference between the envelope maxima of 24 cm.^{-1} ; this degree of resolution was not attained with the fluorite prism in our possession; defects in the actual sample may be responsible for this failure, and generally with this prism and spectroscope, separable wave-numbers are 50 per cent. further apart than those given in the table.

Table II enables us to contrast the prism with the grating, and to show where the former may give the desired experimental data even more readily than the

* See Czorny, *loc. cit.*

† 'J. Opt. Soc. Amer.,' vol. 15, p. 257 (1927).

later. Two factors have to be considered in infra-red measurements, viz., the resolving power of the instrument and the energy falling on the thermopile. The resolving power, $\lambda/d\lambda$, of the grating is greater than that of the prism at all wave-lengths; at longer wave-length, however, a given frequency difference corresponds to a much larger wave-length difference than at shorter wave-lengths and the large resolving power is not essential; in fact, $d\lambda \propto \lambda^2 d\nu$. The prism spectrometer at any given wave-length presents to the thermopile a greater amount of energy than a grating spectrometer. Hence, between 8 and 22 μ , where the available energy is very low, the prism spectrometer may give useful data more readily than a grating instrument.

Finally, Table III gives the moment of inertia corresponding to a definite Bjerrum separation; it is useful since it indicates those molecules whose bands should be carefully examined.

Table III.

$\Delta\nu$ (cm. ⁻¹)	70	50	20	13	9	8	7	6	5	4
J.g. cm. ² $\times 10^{28}$	0.1	0.2	1.1	2.6	5.5	7.0	9.0	12	18	28

In order to bring out the full resolving power of the instrument, it is essential to make observations at sufficiently frequent intervals; four or six per slit width allow of this. 0.01 of a revolution of the wave-length drum moves the image of the spectrum line 0.0022 inch; hence, when examining a band with a slit width of 0.01 inch, 90 to 120 readings have to be taken per revolution of the micrometer drum.

Investigations in the Infra-Red Region of the Spectrum.
Part II.—The Absorption Spectrum of Sulphur Dioxide.

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London.

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It has been pointed out that if the precautions indicated in the previous paper are carefully observed, a high order of accuracy in infra-red measurements can be obtained with a prism spectrometer. Although the final word at present rests with the grating instrument on account of its higher resolving power, nevertheless a deal of useful work remains to be done with prisms. A band can be located (generally a necessary process for a prism spectrometer before the grating can be applied), the band centre and band type can often be determined, and the molecular constants can be approximately deduced.

It is proposed in these papers to examine the spectra of gases and vapours in which the molecule has three different moments of inertia. The rotational fine structure within a vibrational band due to an asymmetrical rotator is very complex and individual lines may lie so close and the constituent series so overlap that absorption may be practically continuous. The prism spectrometer enables the first step in the unravelling of the tangle to be accomplished, in that the envelope of the individual lines gives under favourable circumstances the branches of the Bjerrum doublets, and hence enables the moments of inertia to be determined and frequently provides a knowledge of what may be called the resultant electrical structure of the molecule.

Experimental.

Sulphur dioxide was taken from a commercial "syphon" and passed slowly through concentrated sulphuric acid into the phosphoric oxide and absorption tube system which had been previously evacuated. When the attached manometer showed a pressure of gas just greater than was required in the absorption tube, the tap connecting the sulphuric acid bubblers to the evacuated system was closed, the sulphur dioxide frozen in a liquid air trap, and the system again pumped out to remove any air that had passed with the gas into the absorption tube. This process was necessary in order to obtain the true pressure of sulphur dioxide in the tube. The liquid air trap was subsequently slowly warmed up until the desired pressure was shown by the manometer; the

trap was then shut off and time allowed for pressure equilibrium to be attained throughout the system which included the glass spiral ; the manometer was again read. The preliminary examination was carried out at a pressure of approximately 65 cm., when the positions and approximate absorptions of all the bands were determined, each band was then investigated individually at a pressure required to give a maximum percentage absorption of approximately 50 per cent. where the resolution of the bands is most readily effected.

The Observed Data.

The details of the bands revealed by this investigation are collected in Table I. The second and third columns give respectively the wave-lengths and wave-numbers of the band centres ; the fourth and fifth columns give the maxima of the band envelope and their separations in wave-numbers ; in the sixth and seventh are to be found the pressure of gas in centimetres of mercury with the maximal percentage absorption. The last three columns give the suggested origin of the band with the calculated value and the discrepancy between this and the observed. Coblenz* explored the spectrum as far as 15 μ with a rocksalt prism and his results are shown in fig. 1. When the individual bands

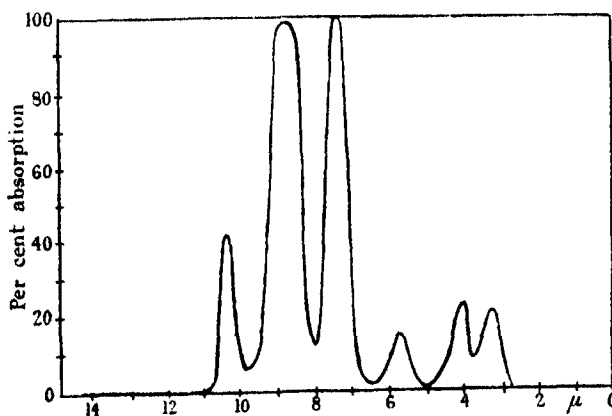


FIG. 1.—The Infra-Red Absorption of SO_2 according to Coblenz.

are considered in detail below, it will be seen that there exist certain unexplained differences between the two sets.

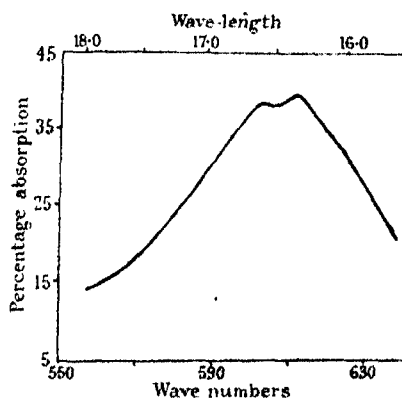
* "Investigations of Infra-red Spectra," Part I, pp. 52 and 177.

Table I.

Band.	Band centre.		Maxima (cm.^{-1}).	P - R $\Delta\nu$ (cm.^{-1}).	Pressure cm. Hg.	Maximal per cent. absorption	Origin.	ν calculated (cm.^{-1}).	Difference $\nu - \nu_0$.
	λ (μ).	ν_0 (cm.^{-1}).							
A	16.494	606	{ 611 602 }	9	63.5	37	ν_1	—	—
B	8.680	1152	{ 1169 1138 }	31	4.6	80	ν_2	—	—
C	7.347	1361	{ 1377 1361 1348 }	30	0.15	55	ν_3	—	—
D	5.345	1871	1871	—	60	12	$\nu_3 + \nu_2 - \nu_1$	1907	36
E	4.338	2305	{ 2317 2288 }	29	64.5	47	$2\nu_2$	2304	-1
F	4.003	2499	2499	—	64.5	89	$\nu_3 + \nu_2$	2513	14

The Individual Bands.

A. *Fundamental Band at 16.494 (± 0.004) μ , $\nu = 606 \text{ cm.}^{-1}$, not observed by Coblenz.*—This band was investigated with the sylvine prism with actual slit widths both of 0.025 inch; a galvanometer deflection of 15 cm. was obtained when the radiation passed through the empty tube. Under these conditions the slit includes 3.5 cm.^{-1} , although the separation obtained in practice is not quite so good. However, reference to fig. 2 will show that a doublet is present; the region near the maxima was re-examined with slits 0.015 inch and the same doublet separation was obtained, viz., 9 cm.^{-1} , the

FIG. 2.—Fundamental Band at 16.5 μ .

band consisting of P and R branches. The doublet minimal percentage absorption observed with the narrower slit widths was only 3 per cent. lower than the maxima on either side, and it was not considered justifiable to assume the real existence of this separation until other possible sources of this small variation with wave-length had been investigated. The most likely cause would be a difference in the transmission of the two tubes at this point; accordingly both tubes were evacuated and the galvanometer throws again read. There was actually a very small difference in the transmissions, but this difference remained accurately constant throughout the range; the tube was then refilled and the doublet again appeared. There is then every justification for adopting the given value for the doublet separation.

B. *Fundamental Band at $8.680 (\pm 0.004) \mu$, $\nu_2 = 1152 \text{ cm.}^{-1}$; Coblenz gives 8.7μ .*—A rocksalt prism was used for this region, with slit widths 0.01 and 0.01 inch, including 10 cm.^{-1} . We have a well-defined doublet of P and R branches only, the separation being 31 cm.^{-1} . The observations in this as in the other bands were repeated at different pressures and with different

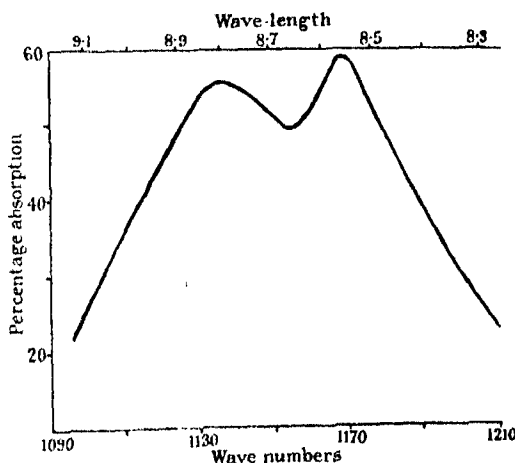


FIG. 3.—Fundamental Band at 8.68μ .

samples of the gas, and the results were consistent. The mean maximum percentage absorption was determined at 0.9 and 4.6 cm. pressure and was found to be 23 and 80 per cent. respectively. The band is shown in fig. 3.

C. *Fundamental Band at $7.347 (\pm 0.002) \mu$, $\nu_3 = 1361 \text{ cm.}^{-1}$ (fig. 4); Coblenz gives 7.4μ .*—This is the most intense band, and Table I enables the intensity relationships between the various bands to be approximately determined. Coblenz shows the two bands at 8.7 and 7.4μ as having the same

intensities; this is probably due to the fact that the maximum absorption in each case is 100 per cent., but there is no doubt that the latter band is much more powerful. It was examined with the fluorite prism, the slit widths being 0.007 inch in each case and including 4 cm.^{-1} ; maxima 6 cm.^{-1} apart should be separated. We have repeated observations on this band many times at different pressures, slit widths, and with different samples of gas; the same qualitative result was obtained in all cases. Reference to fig. 4 will show what appear to be P, Q and R branches, and by reducing the slit

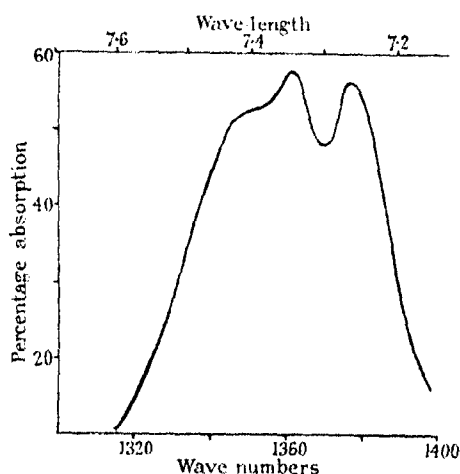


FIG. 4.—Fundamental Band at 7.3μ .

width as low as 0.004 inch it was hoped to effect a more complete separation of the Q and P, but the figure shows the ultimum of resolution under the given conditions. The value of the band centre given by the authors in a preliminary note to 'Nature,'* was that of the minimum between the Q and R branches, viz., 7.301μ ; theoretical considerations have since confirmed the suggestion that the band has a strong Q branch and this is now given as the band centre. The pressure 0.15 cm. of mercury given in the table must be taken as indicative of the order of magnitude since the presence of the glass spiral renders the determination of low pressures somewhat difficult; at any pressures comparable with those used for the other bands the galvanometer deflections were negligible.

D. *Combination Band at $5.345 (\pm 0.002) \mu$, $\nu = 1871 \text{ cm.}^{-1}$.*—A very weak band explored with the fluorite prism and slit widths of 0.005 inch (includes 8 cm.^{-1} and resolves 12 cm.^{-1}). Only one maximum was observed, chiefly

* Vol. 126, p. 59 (1930).

because of the low absorption; to avoid the possibility of the presence of "false band" the tubes were tested for inequality of transmission as before, and the gas samples were varied. Coblenz reports a band at 5.68μ , with a maximal percentage absorption of 15 to 20 per cent. in a cell length of 6.3 cm. at atmospheric pressure; it is difficult to say whether the two are identical, our band is certainly much weaker. The formulation $\nu_2 + \nu_3 - \nu_1$ fits the band centre better than any other; the discrepancy of 36 cm.^{-1} may be attributed to the anharmonicity of the combination. The low intensity is in accord with the existence of a difference tone which is not unexpected, as one quantum of radiation of frequency 606 cm.^{-1} is 10×10^{-14} ergs., whilst the kinetic energy of translation of the molecule at 17° C. is 4×10^{-14} ergs. There is, however, the possibility that this band is to be interpreted as the combination of the fundamental at 7.34μ with a two-parameter band whose ground level is at 606 cm.^{-1} , of the type $\nu_2 + (2 - 1)\nu_1$; our experimental evidence does not allow us to say whether $(2 - 1)\nu_1$ exists.

E. *Combination Band at $4.338 (\pm 0.003) \mu$, $\nu = 2305 \text{ cm.}^{-1}$ (fig. 5).*—Coblenz shows a band at 3.97μ ; this has probably been resolved in the present

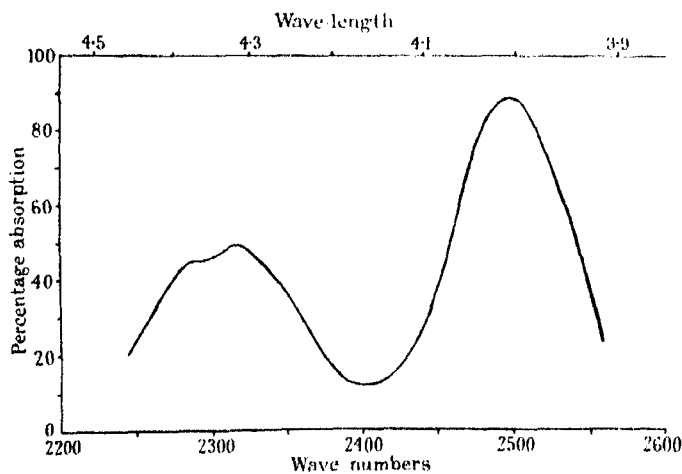


FIG. 5.—Combination Bands at 4.35μ and 4.0μ .

work into the bands 4.34 and 4.00μ (see below). The fluorite prism with slit widths 0.007 in each case was employed, the thermopile slit includes 12 cm.^{-1} and maxima separated by 18 cm.^{-1} resolved. Two indistinct maxima 29 cm.^{-1} apart were distinguished and the band appears to consist of P and R branches; it is apparently the first harmonic of the second fundamental, ν_2 ; the calculated and observed values are exceptionally close.

F. *Combination Band* at $4.003 (\pm 0.003) \mu$, $\nu = 2499 \text{ cm.}^{-1}$ (*fig. 5*).—This band was resolved by Meyer, Bronk, and Levin into P and R branches by means of a grating, the band centre, as far as one can judge from the very small figure provided, being at or near 4.001μ (2502 cm.^{-1}).^{*} The separation of the maxima obtained by the above authors was 24 cm.^{-1} ; we have failed to resolve this band, although this value appears to be just within the limits of possible resolution for the fluorite prism at the wave-length in question. The frequency calculated on the assumption that this band is represented by $\nu_2 + \nu_3$ is in good agreement with that observed.

The Sulphur Dioxide Molecule.

The existence of a permanent electric moment[†] indicates a triangular structure for this molecule; the infra-red data given above are in accordance with this assumption; we have three distinct fundamental frequencies resolvable into P and R or P, Q, and R branches. From the maximal separation in the Bjerrum doublets the classical values for possibly two of the moments of inertia of the molecule are easily calculated. If we accept the separations of 31 and 9 cm.^{-1} , the corresponding moments of inertia are 4.7 and $55 \times 10^{-39} \text{ g. cm.}^2$; the molecule has, however, three finite and unequal moments of inertia and we are therefore not entitled to assume that these are the moments about any two perpendicular axes. If a , b and c are the reciprocals of the principal moments of inertia of sulphur dioxide, where $a < b < c$, the observed moments of inertia may have values whose reciprocals are given by $(a + b)/2$, $c - (a + b)/2$, c , a and $(c - a)/2$.[‡] Identification of the observed moments of inertia with the correct combinations of the principal moments of inertia is only possible when we have a knowledge of the orientation in the molecule of the different electric moments effective in the different bands; selection rules then guide us in the process.

Bjerrum[§] seems to have been the first to investigate theoretically the fundamental frequencies due to triatomic molecules of isosceles triangular form. He assumed the forces acting between the atomic centres to be perfectly elastic and calculated the fundamental frequencies in two cases: (1) where the restoring forces are central, and (2) where the restoring force between S and O is central, and a restoring couple acts about an axis passing through the S atom

^{*} 'J. Opt. Soc. Amer.,' vol. 15, p. 257 (1927).

[†] Zahn, 'Phys. Rev.,' vol. 27, p. 455 (1926).

[‡] See Bailey, Cassie and Angus, 'Trans. Faraday Soc.,' vol. 26, p. 197 (1930).

[§] 'Verhand. Deutsche Physikal. Gesell.,' vol. 16, p. 737 (1914).

and perpendicular to the molecular plane ; the latter couple replaces the central restoring force acting between the oxygen atoms in case (1). Clearly Bjerrum's calculations are only a first approximation ; the method has been amplified and extended.* It is nevertheless invaluable in assigning the different fundamental frequencies to different modes of vibration of the molecule, and is the general mathematical method employed in vibration problems. The determinant equation which gives the possible frequencies is a cubic ; the relations between the roots of the equation and its coefficients give three equations in terms of the two elastic coefficients, the semi-angle, $\alpha/2$, of the isosceles triangle, the masses of the atoms, and the periods of the normal modes of vibration. The elastic coefficients can be eliminated to give an equation in the masses of the atoms, the periods of the normal modes, and α : it is a quadratic in $\cos^2 \alpha/2$. There are hence six possible values for $\cos^2 \alpha/2$ corresponding to the three permutations of the three periods ; four of these are imaginary, and we have left two possible values of α . These are found to be approximately 40° and 140° , and we finally arrive at four solutions in all : two correspond to case (1) which with Bjerrum we shall refer to as a system of central forces, and two to case (2) which we shall call a system of valence forces. The relative amplitudes of vibration for the three atoms can also be calculated ; the smaller value of α gives vibrations that are almost alike for the central restoring force and for the valence force systems ; the larger value gives different modes in each case (figs. 6 and 7).

The nature of the optical absorption in the infra-red depends on the orientation of the vibrating electric doublet and on the magnitude of its vibration ; the greater the amplitude of vibration of the electric doublet the greater is the percentage absorption. It is here taken as proportional to the vector sum of the amplitudes of vibration of the individual atoms.† If the central force system is chosen, the shortest and longest fundamental periods of vibration correspond to a vibrating electric doublet lying along the bisector of the vertical angle ; and the other period to an electric doublet parallel to a line lying in the plane of the triangle and perpendicular to this bisector. The amplitude of the shortest period vibration is much greater than that of the largest ; that is, the shortest wave-length infra-red absorption band should be considerably more intense than the longest. The larger angle model with central forces has these intensities reversed. The valence force system with the larger

* Dennison, 'Astrophys. J.,' vol. 62, p. 84 (1925) and 'Phil. Mag.,' vol. 1, p. 195 (1926) Hund, 'Z. Physik,' vol. 31, p. 81 (1925) and vol. 43, p. 805 (1927).

† Dennison, 'Phil. Mag.,' *loc. cit.*

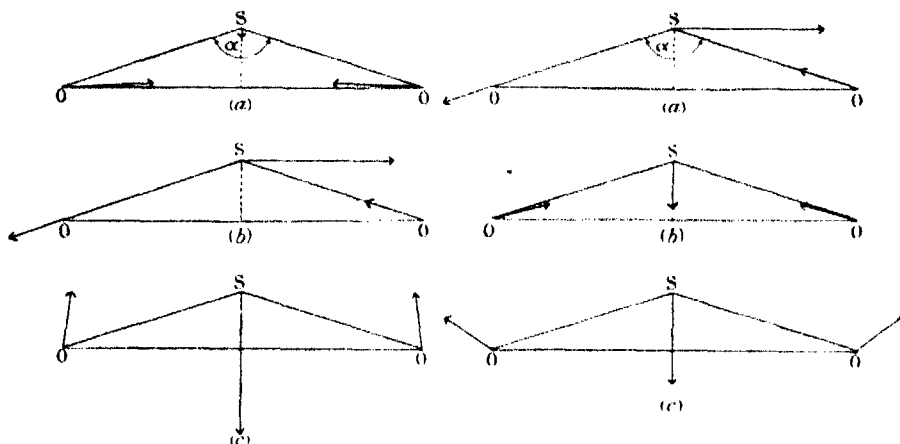


Fig. 6.—System of Central Forces $\alpha=140^\circ$. Fig. 7.—System of Valence Forces, $\alpha=140^\circ$.
 (a) $\lambda = 7.3 \mu$; symmetrical. (a) $\lambda = 7.3 \mu$; asymmetrical.
 (b) $\lambda = 8.68 \mu$; asymmetrical. (b) $\lambda = 8.68 \mu$; symmetrical.
 (c) $\lambda = 16.5 \mu$; symmetrical. (c) $\lambda = 16.5 \mu$; symmetrical.

value for α interchanges the directions of the electric doublets effective in the two shorter periods, and the amplitude of the two longer periods are approximately equal.

The ratios of the experimentally observed intensities cannot be accurately determined as different pressures were required for observations in the different bands. The shortest wave-length band is by far the most intense; the middle band has approximately a maximal percentage absorption of 80 per cent. at 4.6 cm., while the longest has an absorption of only 37 per cent. at 63.5 cm. pressure. The great absorption of the shortest wave-length band compared with the others agrees only with the smaller value of α when the central force system is assumed. On the other hand, the large percentage absorption of the 8.68 μ band compared with that of the 16.5 μ band does not agree with the approximately equal absorptions predicted by the valence force system when the larger value of α is assumed. Thus we see that the intensity relationships of the fundamental bands leave one possible solution for α , namely, that α must be small.

Our model of the sulphur dioxide molecule is, therefore, qualitatively that shown in fig. 8. The shortest and longest wave-length bands have effective electric doublets whose changes during vibration lie along the bisector of the vertical angle; the middle wave-length band has an effective electric doublet whose changes lie wholly normal to this line, and in the plane of the triangle.

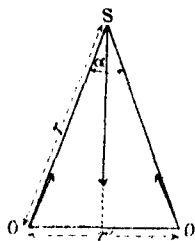


FIG. 8A.—Fundamental at 7.3μ ; symmetrical.

$\alpha = 24^\circ$. $r = 4.8 \times 10^{-8}$ cm. $r' = 2 \times 10^{-8}$ cm.

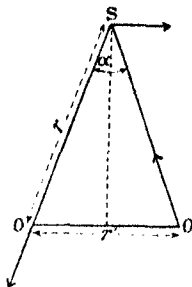


FIG. 8B.—Fundamental at 8.68μ ; asymmetrical.

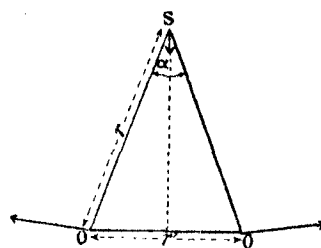


FIG. 8C.—Fundamental at 16.5μ ; symmetrical.

The orientation of the change in electric moment is now known, and an interpretation of the branch separations is possible.

Band B at 8.68μ is a simple doublet. The electric moment effective in the absorption is normal to the bisector of the vertical angle; hence there should be no Q branch corresponding to spin about this axis, and the P and R branch separation gives the moment of inertia about this principal axis, *i.e.*, the least moment of inertia. The doublet separation is 31 cm.^{-1} , and the corresponding moment of inertia is $4.7 \times 10^{-39} \text{ g. cm.}^2$.

Band A at 16.5μ is a simple doublet containing a P and R branch. The effective electric doublet is parallel to the bisector of the vertical angle or axis of least inertia. There should, therefore, be no separation corresponding here to the least moment of inertia, we must have a separation which corresponds either to the greatest moment of inertia or to the arithmetic mean of the greatest and intermediate principal moments of inertia according as the molecule spins about the axis of greatest or least inertia. Since the difference between the greatest and intermediate moments of inertia is small compared with the value of either, the difference between these effective moments of inertia is negligible. We therefore assume the separation of 9 cm.^{-1} to correspond to the largest moment of inertia; its value is $55 \times 10^{-39} \text{ g. cm.}^2$.

Band C at 7.35μ presents some difficulties. This band arises from an effective electric doublet parallel to the least axis of inertia. There should therefore be no P and R separation corresponding to the least moment of inertia; on our model the band should be similar to that at 16.5μ . The observed band, however, has P and R branches separated by 29 to 30 cm.^{-1} , with a strong Q branch; the general form of the band, as shown by our resolution and by Coblenz's original diagram, makes it unlikely that we are dealing with two superimposed bands, although this possibility has always to

be borne in mind, and study of the band with apparatus of higher resolving power has to be made before complete certainty is reached. The fact that the doublet separation does correspond with the smallest moment of inertia admits of interpretation if we assume that the change in the effective electric doublet is not wholly parallel to the least moment of inertia. The very great intensity of the band compared with that at 16.5μ makes this supposition plausible; for Bjerrum's simple hypotheses and Dennison's assumption may be almost correct for the small amplitudes involved in the 16.5μ vibration, and be no more than rough approximations for such large amplitudes as occur in the 7.35μ band. The P and R branches are therefore assumed to be due to changes in rotation about the least axis of inertia. Since the Q branch has a greater intensity than either of the others, the effective electric doublet must have a larger component parallel to the least axis of inertia than perpendicular to it.

Band E at 4.34μ is the first harmonic of the band at 8.68μ and its characteristics tally with this assignment.

Band F at 4.00μ has been resolved into P and R branches by Meyer, Bronk and Levin (*loc. cit.*). In assigning this band to a combination tone $\nu_2 + \nu_3$ of the fundamentals at 8.68 and 7.45μ , we should have an effective electric doublet inclined to the axes of least and intermediate moments of inertia, but perpendicular to the axis of greatest. The separation of the P and R branches is given as 24 cm.^{-1} , which corresponds to a moment of inertia of $7.7 \times 10^{-39} \text{ g. cm.}^2$. This value does not fit any of the theoretically possible combinations of the principal moments of inertia (55 , 50 and $4.7 \times 10^{-39} \text{ g. cm.}^2$). In the very small diagram provided, the authors show a curve with a very broad P branch compared with those we have observed; the moment of inertia must depend on the amplitude of vibration of the atoms, and there is in fact no reason to assume that the moment of inertia given by the fundamental bands should in all cases be the same as that given by the harmonics or combination tones. It is even possible that the difference in values in the two cases might be used to deduce the ratio of the amplitudes of the atomic vibrations in a fundamental and combination tone.

A quantitative model based on the supposition that 55 and $4.7 \times 10^{-39} \text{ g. cm.}^2$ are the greatest and least principal moments of inertia offers the following characteristics:—

- (i) $\text{S} - \text{O} = 4.8 \times 10^{-8} \text{ cm.}$
- (ii) $\text{O} - \text{O} = 2.0 \times 10^{-8} \text{ cm.}$
- (iii) $\hat{\text{OSO}} = 24^\circ.$

This model with the above interpretation of the fundamental vibrations is supported by the work of Hund (*loc. cit.*). He derived expressions for the frequencies of vibration of the water molecule, and his method is applicable to sulphur dioxide. We make the following assumptions: (i) sulphur loses four electrons, two to each atom of oxygen; (ii) the atom of sulphur has a constant polarisability; (iii) it attracts the oxygen atoms according to Coulomb's law, and repels them inversely as the fifth power of the distance S — O; (iv) the oxygen atoms repel each other according to Coulomb's laws. The constant polarisability and the charge effective in the S — O inverse fifth power repulsion are eliminated by means of the equations determining the configuration of stable equilibrium. Thence, following Hund's calculation, the frequencies of the unsymmetrical and symmetrical vibrations are given by the expressions

$$\omega_s^2 = \left(\frac{1}{m} + \frac{2}{M} \sin^2 \alpha \right) (A_{11} - A_{12}); \quad (1)$$

and

$$\omega_{1,3} = p \pm \sqrt{(p^2 - q)}; \quad (2)$$

where

$$p = \frac{\cos^2 \alpha}{M} (A_{11} + A_{12}) + \frac{1}{2m} (2A_{00} + A_{11} + A_{12} + 4A_{01} \sin \alpha);$$

$$q = \cos^2 \alpha \left(\frac{1}{m^2} + \frac{2}{mM} \right) [2A_{00} (A_{11} + A_{12}) - 4A_{01}^2];$$

and

$$A_{00} = \frac{3e^2}{s^3}, \quad A_{01} = -\frac{3e^2}{rs^2}, \quad A_{11} = \left(\frac{8}{r^3} + \frac{7}{s^3} - \frac{3}{r^2s} \right) e^2, \quad A_{12} = \left(\frac{9}{2r^2s} - \frac{3}{s^3} \right) e^2;$$

in which M = mass of sulphur atom; r = length of side of triangle; m = mass of oxygen atom; s = length of base of triangle; α = semi-vertical angle of triangle.

On insertion of the appropriate values as determined above, the ratios of the three frequencies appear as

$$13.4 : 11.4 : 6.6,$$

where the middle value represents the unsymmetrical vibration, or that vibration whose effective electric doublet is normal to the axis of least inertia. The observed frequency ratios are as

$$13.6 : 11.4 : 6.1,$$

the middle value corresponding to the vibration whose effective electric doublet was assumed normal to the axis of least inertia.

Comparison with the Original Observations of Coblentz.

Coblentz's original curve (fig. 1) shows a number of unresolved bands; we are unable to obtain bands corresponding to those at 3.18 and 10.37μ , while in place of the band at 5.68μ we have another at 5.34μ . Coblentz prepared his gas by acting on sodium bisulphite with strong sulphuric acid, and purified it by subsequent fractional liquefaction and distillation without eliminating any of the observed bands. Most careful search has failed to reveal the missing bands; we have had constructed tubes of stainless steel, 1 metre in length, and are proposing to examine the absorption spectra of a number of gases under pressure; in this way we hope to add to the known bands of these gases and hence obtain further information regarding the molecular constants. Our search for the missing bands was made under pressures of 63 cm. of mercury with a column of gas 45 cm. long, and it seems likely that we should have observed them if they had been present inasmuch as Coblentz used a 6.3 cm. cell under 74.4 cm. pressure. Our gas was taken from the commercial "syphon," but the presence of any impurities would be more likely to add to the number of bands than to diminish them. It is of importance to point out that Coblentz noticed that the wave-number difference between his bands at 3.18 and 3.97μ was 605 cm.^{-1} (miscalculated, should be 626 cm.^{-1}) and between those at 5.68 and 8.70μ was 612 cm.^{-1} . The closeness of these differences to the first fundamental at 606 cm.^{-1} would indicate a positive existence for the missing bands; in that case $3.18 \mu = 3145 \text{ cm.}^{-1}$ is $\nu_1 + \nu_2 + \nu_3$ (calculated from our results, 3109 cm.^{-1}); $5.68 \mu = 1762 \text{ cm.}^{-1}$ is $\nu_1 + \nu_2$ (calculated 1758); and $10.37 \mu = 965 \text{ cm.}^{-1}$ might be $2\nu_2 - \nu_1$ (calculated 944 cm.^{-1}), although the comparatively great intensity (40 per cent. maximum absorption) of this band is against this assumption.

The Raman Spectrum of Sulphur Dioxide.

The Raman spectrum of solutions of sulphur dioxide in water, carbon tetrachloride and other solvents has been determined by Harkins, Gans and Bowers;* they obtained prominent lines at 1150 and 1114 cm.^{-1} . Dickinson and West† repeated this work with liquid sulphur dioxide, and observed several lines corresponding to infra-red frequencies of 1146 (very strong) 1340 (medium and diffused), and 524 cm.^{-1} (weak and diffused), but 1114 cm.^{-1} was missing. We can identify all of these except the last as in Table II below.

* 'Nature,' vol. 125, p. 464 (1930).

† 'Phys. Rev.,' vol. 35, p. 1126 (1930).

Table II.—The Raman and Infra-red Frequencies of Sulphur Dioxide.

Raman spectrum.	Infra-red spectrum.	Origin.	Calculated.
cm. ⁻¹ 1146 1340 524	cm. ⁻¹ 1152 1361 —	ν_2 ν_3 $\nu_2 - \nu_1$	cm. ⁻¹ — — 546

The Molecular Constants.

Until other combination- and over-tones have been obtained by an examination of the absorption of the gas under greater pressures, it is not possible to assign definite values to all the characteristics of the molecule; these include the true vibration frequencies and the constants indicating the measure of anharmonicity in the various modes. We can, however, say at once from bands B and E that $a_2 + b_2$ is 1152 cm.⁻¹, and that $2a_2 + 4b_2$ is 2305; it follows then that a_2 is 1152 cm.⁻¹, and that b_2 is zero within the limits of experimental error, which is in keeping with the large moment of inertia. The difficulties encountered above in the analysis of band C place some doubt upon the value of the band centre, and further resolution must be awaited before a definite pronouncement can be made as to the values of a_3 and b_3 . On the assumption then that band C contains a pronounced Q branch, the recognised constants of the sulphur dioxide molecule can be summarised as in Table III.

Table III.—The Molecular Constants of Sulphur Dioxide.

Moments of inertia in g. cm. ² $\times 10^{30}$.	Lengths of side in cm. $\times 10^8$.	Vibration frequencies in cm. ⁻¹ .
$J_1 = 55$ $J_2 = 50$ $J_3 = 4.7$ $J_1 = J_2 + J_3$	S — O = 4.8 O — O = 2.0 whence angle OSO = 24°	$a_1 + b_1 = 606$ $a_2 = 1152, b_2 = 0$ $a_3 + b_3 = 1361$

Summary.

1. The infra-red absorption spectrum of sulphur dioxide has been re-examined in the region 1 to 22 μ with a prism spectrometer fitted with quartz, fluorite, rocksalt, and sylvine prisms.
2. The spectrometer having been carefully calibrated and allowance made

for the change in dispersion of the prism materials with temperature, it is believed that the results are generally accurate to $\pm 0.003 \mu$.

3. The ascertained spectrum has been compared with the previous work of Coblentz.

4. The partial resolution effected in most of the bands has rendered possible the determination of a number of the molecular constants, in particular the size and shape of the molecule, the moments of inertia, and the fundamental vibrational frequencies.

5. The observed infra-red spectrum has been co-ordinated with the Raman spectrum of the liquid.

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The Tidal Oscillations in an Elliptic Basin of Variable Depth.

By G. R. GOLDSBROUGH, F.R.S.

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§ 1. *Introduction.*

The problem of the "long" waves in a circular basin of uniform depth involves in its solution a transcendental function*—the Bessel function, and the determination of the free periods requires a knowledge of the zeros of this function or an allied function. On the other hand, when the basin, still circular, has a certain variable depth,† it was shown by Lamb that the solution is expressed in terms of simple algebraic polynomials and the free periods of oscillation are expressed by an extremely simple formula.

In similar fashion, the solution of the problem of the "long" waves in an elliptic basin of uniform depth involves the use of elliptic cylinder functions, and the free periods are only obtained as the result of lengthy numerical approximations.‡

The present paper examines the oscillations in an elliptic basin having a paraboloidal law of depth such that, when the eccentricity vanishes, the basin has the same form as that discussed by Lamb. It is found in this case that the problem is again soluble in terms of polynomials and the free periods of any type of motion can be found with comparative ease. The simple form of the results makes it possible to examine the general character of the oscillations without great complication.

The analysis is also interesting in that it affords a physical interpretation of certain theorems concerning the nature of the solutions of differential equations.

The results obtained should have an application in the theory of *seiches* in lakes where the motion cannot be accurately taken as longitudinal.

* Lamb, "Hydrodynamics," 4th ed., p. 277.

† *Ibid.*, p. 283.

‡ Jeffreys, 'Proc. Lond. Math. Soc.,' vol. 23, p. 455 (1923); Goldstein, *ibid.*, vol. 28, p. 91 (1928).

§ 2. *Statement of the Equation .*

Consider the long waves in an elliptic basin of variable depth h . We form the equations in elliptic co-ordinates ξ, η , by means of the transformation

$$\begin{aligned}x &= c \cosh \xi \cos \eta, \\y &= c \sinh \xi \sin \eta.\end{aligned}$$

Then, if u, v are the velocity components in the new system, we may write for simple-harmonic vibrations of period $2\pi/\lambda$,

$$\left. \begin{aligned}Hu &= \frac{ig}{\lambda} \frac{\partial \zeta}{\partial \xi}, \\Hv &= \frac{ig}{\lambda} \frac{\partial \zeta}{\partial \eta},\end{aligned} \right\} \quad (1)$$

where ζ is the displacement of the free surface at the point (ξ, η) and $H^2 = c^2 (\cosh^2 \xi - \cos^2 \eta)$. The corresponding equation of continuity is

$$\frac{\partial}{\partial \xi} (hHu) + \frac{\partial}{\partial \eta} (hHv) + H^2 \lambda \zeta = 0. \quad (2)$$

On eliminating u and v from (1) and (2) we have the equation

$$\frac{\partial}{\partial \xi} \left(h \frac{\partial \zeta}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(h \frac{\partial \zeta}{\partial \eta} \right) + H^2 \lambda^2 \zeta / g = 0. \quad (3)$$

We shall choose as the law of depth

$$h = h_0 (a - \cosh^2 \xi) (a - \cos^2 \eta), \quad (4)$$

where $a = \cosh^2 \xi_0$ and $\xi \leq \xi_0$.

The surface of the lake is then bounded by the ellipse $\xi = \xi_0$ which has axes $2c \cosh \xi_0, 2c \sinh \xi_0$. Further, the law of depth (4) reduced to rectangular co-ordinates gives

$$h/h_0 = a^2 - a - \frac{x^2}{c^2} (a - 1) - y^2 \frac{a}{c^2}. \quad (5)$$

Hence the contour of the lake is paraboloidal in form and the greatest depth is $h_0 (a^2 - a)$, or $h_0 \cosh^2 \xi_0 \sinh^2 \xi_0$.

On substituting (4) in (3) we have the resulting equation

$$\begin{aligned}(a - \cos^2 \eta) \frac{\partial}{\partial \xi} (a - \cosh^2 \xi) \frac{\partial \zeta}{\partial \xi} + (a - \cosh^2 \xi) \frac{\partial}{\partial \eta} (a - \cos^2 \eta) \frac{\partial \zeta}{\partial \eta} \\ + \frac{\lambda^2 c^2}{gh_0} (\cosh^2 \xi - \cos^2 \eta) \zeta = 0. \quad (6)\end{aligned}$$

Then, if ζ may be expressed in the form XY , where X is independent of η and Y is independent of ξ , equation (6) breaks up in the usual way into the two ordinary equations

$$\left. \begin{aligned} \frac{d}{d\xi}(a - \cosh^2 \xi) \frac{dX}{d\xi} + \frac{1}{4}\kappa^2 X \{1 - k^2(a - \cosh^2 \xi)\} &= 0, \\ \frac{d}{d\eta}(a - \cos^2 \eta) \frac{dY}{d\eta} + \frac{1}{4}\kappa^2 Y \{-1 + k^2(a - \cos^2 \eta)\} &= 0, \end{aligned} \right\} \quad (7)$$

where k^2 is an undetermined constant and κ^2 is written for $\lambda^2 c^2 / gh_0$.

If in the first equation of (7) we put $\xi = \eta$ it reduces to the second. Hence from the solution of one equation we may easily infer that of the other.

The only other conditions to be fulfilled are that $hu, hv \rightarrow 0$ at the edge of the lake $\xi = \xi_0$. Since $\cosh \xi_0 > 1$, H does not vanish anywhere at the boundary. These conditions are then satisfied if ζ has its first derivatives finite at $\xi = \xi_0$, for all values of η . The forms of the solutions adopted in the succeeding sections are in accordance with this requirement.

§ 3. Discussion of Equation (7).

In the second of equations (7) put $z = \cos^2 \eta$, $Y = w$, $\frac{1}{4}\kappa^2(1 - k^2a) = \sigma\tau$ and $\frac{1}{4}\kappa^2 k^2 = -\sigma\tau$. The equation then becomes

$$\frac{d^2 w}{dz^2} + \frac{dw}{dz} \left(\frac{1}{z} + \frac{1}{z-1} + \frac{1}{z-a} \right) + \frac{w\sigma\tau(z-q)}{z(z-1)(z-a)} = 0. \quad (8)$$

This equation has four regular singularities which with their corresponding exponents are given by the following scheme :

$$\begin{Bmatrix} 0 & 1 & a & \infty \\ 0 & 0 & 0 & \sigma \\ \frac{1}{2} & \frac{1}{2} & 0 & \tau. \end{Bmatrix}$$

And since the sum of the exponents for this equation is 2 we have $\tau = 1 - \sigma$.

Equation (8) is a particular case of the equation discussed by Heun.* It is obtainable from the general equation of the second order with five singularities (one at infinity) by the confluence of one of the finite singularities with that at infinity. For instance, the general equation of the second order with five regular singularities at a_1, a_2, a_3, a_4 and ∞ respectively may be written†

$$\frac{d^2 w}{dz^2} + \left\{ \sum_{r=1}^4 \frac{1 - \alpha_r - \beta_r}{z - a_r} \right\} \frac{dw}{dz} + \left\{ \sum_{r=1}^4 \frac{\alpha_r \beta_r}{(z - a_r)^2} + \frac{Az^2 + 2Bz + C}{\prod_{r=1}^4 (z - a_r)} \right\} w = 0. \quad (9)$$

* 'Math. Annalen,' vol. 33, p. 161 (1889).

† Whittaker and Watson, "Modern Analysis," 3rd ed., p. 203.

In this equation, the exponents at a_r are α_r , β_r and A , B , C are constants.

If now in equation (9) we put

$$\begin{aligned} a_1 &= 0, & a_2 &= 1, & a_3 &= a, \\ \alpha_1 &= \alpha_2 = \frac{1}{2}, & \alpha_3 &= 0, & \beta_r &= 0 \quad (r = 1, 2, 3, 4) \\ A &= \sigma\tau, & 2B &= -\sigma\tau(q - a_4), & C &= -a_4q\sigma\tau, \end{aligned}$$

and let $a_4 \rightarrow \infty$, equation (9) reduces at once to equation (7).

Equation (8) is similar to Lamé's equation. The only difference lies in the fact that (8) has a double zero exponent at the singularity a . The method of procedure used in dealing with Lamé's equation in its algebraic form may be applied at once to (8).

If the solution of (8) valid in the vicinity of $z = 0$ be expressed as

$$\zeta = F(a, q; \sigma, 1 - \sigma; \frac{1}{2}, \frac{1}{2}, 0; z), \quad (10)$$

then it is readily shown in the usual way that

$$\zeta = z^{\frac{1}{2}} F(a, q; \sigma + \frac{1}{2}, \frac{3}{2} - \sigma; \frac{3}{2}, \frac{1}{2}, 0; z), \quad (11)$$

$$\zeta = z^{\frac{1}{2}} (z - 1)^{\frac{1}{2}} F(a, q; \sigma + 1, 2 - \sigma; \frac{3}{2}, \frac{3}{2}, 0; z), \quad (12)$$

and

$$\zeta = (z - 1)^{\frac{1}{2}} F(a, q; \sigma + \frac{1}{2}, \frac{3}{2} - \sigma; \frac{1}{2}, \frac{3}{2}, 0; z) \quad (13)$$

are also solutions.

These forms give the different types of motion.

§ 4. *Solution of Equation (8).*

It is known that an equation of type (8) has a solution in the form of a polynomial for appropriate values of σ and q . To determine these, assume a solution in the vicinity of the point $z = 0$ in the form

$$w = \Sigma C_n z^{p+n},$$

where the exponent $p = 0$ or $\frac{1}{2}$. On substituting in equation (8), we have the following relation between the constants C where n is any integer.

$$\begin{aligned} C_{n+1} a \{ (p + n + 1)(p + n + \tfrac{1}{2}) \\ + C_n \{ -\sigma(1 - \sigma)q - (p + n)^2(1 + a) - \tfrac{1}{2}(p + n) \} \\ + C_{n-1} \{ (p + n)(p + n - 1) + \sigma(1 - \sigma) \} \} = 0. \end{aligned} \quad (14)$$

If we choose $\sigma = p + m$, m being an integer, it may be shown* that q is then the root of an algebraic equation of degree m and also that the corresponding polynomial solution is of order $(m - 1)$. Further, with the conditions as in the present problem, the roots q are all real and distinct.

By taking $p = 0, \frac{1}{2}$ we arrive at polynomial solutions corresponding to (10) and (11).

Since the solutions have this form, the boundary condition is at once fulfilled.

For the forms (12) and (13) the sequence-relation between the constants C is given by putting $p = 0, \frac{1}{2}$ in the equation

$$\begin{aligned} C_{n-1} \{ (p+n-1)(p+n+1) + \sigma(1-\sigma) + \frac{1}{4} \} \\ + C_n \{ - (a+1)(p+n)^2 - (a+\frac{1}{2})(p+n) - (a/4) - \sigma(1-\sigma)q \} \\ + C_{n+1} a \{ (p+n+1)(p+n+\frac{1}{2}) \} = 0. \end{aligned} \quad (15)$$

The polynomial solution in this case is obtained by putting $\sigma = p + m + \frac{1}{2}$, m being integral.

The second solution associated with any one of the above polynomial solutions is, in general, a transcendental function involving a logarithm.

It has been shown by Stieltjes† that if the equation

$$\frac{d^2 w}{dz^2} + \frac{dw}{dz} \sum_{r=1}^n \frac{a_r}{x - e_r} + \frac{\psi(z)}{\prod_{r=1}^n (x - e_r)} w = 0, \quad (16)$$

where $\psi(z)$ is a polynomial of suitable form, the constants e_r are real and distinct from one another and the constants a_r are real and positive, has a polynomial solution $\phi(z)$, then all the roots of $\phi(z) = 0$, considered as a function of z , are real and lie between the greatest and least of the quantities e_r . In the case of equation (8), these necessary conditions are fulfilled. If, therefore, w_{m-1} is a polynomial solution of (8) of order $(m - 1)$ then w_{m-1} vanishes for $(m - 1)$ values of z lying between 0 and a , and we may write

$$w_{m-1} = (z - z_0)(z - z_1) \dots (z - z_{m-1}).$$

The complete solution of (6) corresponding to this will be

$$\begin{aligned} \zeta = (\cosh^2 \xi - z_0) (\cosh^2 \xi - z_1) \dots (\cosh^2 \xi - z_{m-1}) \\ \times (\cos^2 \eta - z_0) (\cos^2 \eta - z_1) \dots (\cos^2 \eta - z_{m-1}). \end{aligned}$$

If

$$z_r > 1, \quad \zeta = 0 \text{ for } \cosh^2 \xi = z_r;$$

and if

$$z_r \leq 1, \quad \zeta = 0 \text{ for } \cos^2 \eta = z_r.$$

* Cf. Whittaker and Watson, "Modern Analysis," p. 556.

† 'Acta Math.,' vol. 6, p. 121 (1885).

The former case corresponds to a nodal ellipse and the latter to a pair of nodal hyperbolas. The polynomial solution of order $(m - 1)$ therefore gives $(m - 1)$ nodal lines of one kind or the other, a pair of hyperbolas being counted as one nodal line.

Stieltjes has further shown that each distribution of the quantities z_r in the intervals 0 to 1 and 1 to a corresponds to a unique set of coefficients in the polynomial $\psi(z)$, or in the case of (8) to a unique determination of q . Now it has just been shown that there are m independent values of q which give a polynomial solution of order $(m - 1)$. To each of these values of q there is a different distribution of the zeros of w_{m-1} , and it is clear that there are m different distributions of them corresponding to the m different values of q . It follows that each mode of vibration involving a polynomial solution of a certain order has the same number of nodal lines, but that the distribution of the lines between the ellipses and hyperbolas is different for each separate frequency of that type.

This result is illustrated in the next section.

§ 5. *The Modes of Oscillation.*

It is of some interest to examine in detail the earlier modes of vibration of the various types.

(i) In (14) put $p = 0$. The relation then becomes

$$C_{n+1} a (n + 1) (n + \frac{1}{2}) + C_n \{ \sigma (\sigma - 1) q - n^2 (1 + a) - \frac{1}{2} n \} \\ + C_{n-1} \{ n (n - 1) - \sigma (\sigma - 1) \} = 0. \quad (17)$$

For the lowest mode of this type take $\sigma = 2$ and $C_2 = C_3 = \dots = 0$.

The equations then become

$$C_0 \cdot 2 \cdot 1 \cdot q + C_1 a \cdot \frac{1}{2} = 0, \\ - C_0 \cdot 2 + C_1 (2 \cdot 1 \cdot q - a - \frac{3}{2}) = 0.$$

From these

$$q = a/4 + \frac{3}{8} \pm \frac{1}{4} \sqrt{(a^2 - a + \frac{9}{4})}, \quad (18)$$

and therefore

$$\kappa^2 = 4\sigma (\sigma - 1) (a - q) \\ = 6a - 3 \mp 2 \sqrt{(a^2 - a + \frac{9}{4})}. \quad (19)$$

The surface level for this type is given by

$$\zeta \propto \left(\frac{c_0}{c_1} + \cosh^2 \xi \right) \left(\frac{c_0}{c_1} + \cos^2 \eta \right).$$

The mode of lower frequency exhibits a pair of nodal hyperbolas and the higher frequency a nodal ellipse.

(ii) Next put $p = \frac{1}{2}$ in (14). The equation then becomes

$$C_{n+1} a (n + \frac{1}{2}) (n + 1) + C_n \{-\sigma (1 - \sigma) q - (n + \frac{1}{2})^2 (1 + a) - \frac{1}{2} (n + \frac{1}{2})\} \\ + C_{n-1} \{n^2 - \frac{1}{4} - \sigma (\sigma - 1)\} = 0. \quad (20)$$

The lowest mode of this type is given by

$$m = 1, \text{ or } \sigma = 3/2 \text{ and } C_1 = C_2 = \dots = 0.$$

The solution is then

$$\begin{aligned} & q = \frac{2}{3} + \frac{1}{3}a, \\ \text{or} & \\ & \kappa^2 = 2(a - 1), \\ \text{and} & \\ & \zeta \propto \cosh \xi \cos \eta. \end{aligned} \quad (21)$$

The surface remains plane and oscillates about the minor axis.

(iii) The next higher mode of the same type is obtained by putting $\sigma = 5/2$, $C_2 = C_3 = \dots = 0$.

Then

$$\begin{aligned} & \kappa^2 = 10a - 7 \pm 4 \sqrt{(a^2 - 2a + \frac{5}{4})}, \\ & \zeta \propto \cosh \xi \cos \eta \left(\frac{c_0}{c_1} + \cosh^2 \xi \right) \left(\frac{c_0}{c_1} + \cos^2 \eta \right). \end{aligned} \quad (22)$$

In this mode, the minor axis is always a nodal line. With the lower frequency there is also a pair of nodal hyperbolas, while with the higher frequency there is a nodal ellipse.

(iv) For modes involving symmetry about the major axis put $p = 0$ in (15). We have then

$$\begin{aligned} & C_{n-1} \{n^2 - \frac{1}{4} + \sigma (1 - \sigma)\} \\ & + C_n \{-n^2 (a + 1) - n (a + \frac{1}{2}) - (a/4) - \sigma (1 - \sigma) q\} \\ & + C_{n+1} a (n + 1) (n + \frac{1}{2}) = 0. \end{aligned} \quad (23)$$

For the lowest mode of this type take $\sigma = 3/2$, $C_1 = C_2 = \dots = 0$.

Then

$$\begin{aligned} & \sigma (\sigma - 1) q = a/4, \\ \text{or} & \\ & \kappa^2 = 2a, \\ \text{and} & \\ & \xi \propto \sinh \xi \sin \eta. \end{aligned} \quad (24)$$

The surface is plane and oscillates about the major axis.

(v) The next mode of the same type is obtained from (23) by putting $\sigma = 5/2$, $C_2 = C_3 = \dots = 0$.

The surface is

$$\zeta \propto \sinh \xi \sin \eta \left(\frac{c_0}{c_1} + \cosh^2 \xi \right) \left(\frac{c_0}{c_1} + \cos^2 \eta \right).$$

For the lower frequency the nodal lines are the major axis and a pair of hyperbolas, while for the higher frequency the nodal lines are the major axis and an ellipse.

(vi) For modes involving symmetry about both axes we put $p = \frac{1}{2}$ in (15). We have then

$$\begin{aligned} C_{n-1} \{ (n - \tfrac{1}{2})(n + \tfrac{3}{2}) + \sigma(1 - \sigma) + \tfrac{3}{4} \} \\ + C_n \{ -(a + 1)(n + \tfrac{1}{2})^2 - (a + \tfrac{1}{2})(\tfrac{1}{2} + n) - (a/4) - \sigma(1 - \sigma)q \} \\ + C_{n+1} a(n + \tfrac{3}{2})(n + 1) = 0. \end{aligned} \quad (25)$$

The lowest mode of this type is obtained by taking $\sigma = 2$, $c_1 = c_2 = \dots = 0$. Whence

$$\left. \begin{aligned} \zeta \propto \cosh \xi \sinh \xi \cos \eta \sin \eta, \\ \kappa^2 = 4a - 2. \end{aligned} \right\} \quad (26)$$

The nodal lines of this type are the major and minor axes.

(vii) The next higher mode of this type will have the form

$$\zeta \propto \cosh \xi \sinh \xi \cos \eta \sin \eta \left(\frac{c_0}{c_1} + \cosh^2 \xi \right) \left(\frac{c_0}{c_1} + \cos^2 \eta \right),$$

involving as nodal lines the two axes and either a pair of hyperbolas or an ellipse according to the frequency.

§ 7. Comparison with the Case of a Circular Basin.

In the limiting case, when $\xi_0 \rightarrow \infty$ and $c \rightarrow 0$ in such a way that $c \cosh \xi_0$ remains finite, the results just obtained should correspond to those for a circular basin. Lamb has shown* that the natural frequencies for a basin of radius r_0 and greatest depth h_0' , the law of depth being $h = h_0'(1 - r^2/r_0^2)$, are given by the formula

$$\frac{\lambda^2 r_0'^2}{g h_0'} = s(4j - 2) + 2j(2j - 2), \quad (27)$$

s being the number of nodal diameters and $(j - 1)$ the number of nodal circles in the mode.

* "Hydrodynamics," 4th ed., p. 283.

For the limiting form of the elliptical case we have

$$r_0 = \frac{1}{2} c e^{\epsilon_0}, \quad a = \frac{1}{4} e^{2\epsilon_0},$$

and therefore from (5)

$$\begin{aligned} h/h_0 &= \frac{1}{16} e^{4\epsilon_0} \left(1 - \frac{4r^2}{c^2 e^{2\epsilon_0}} \right) \\ &= \frac{1}{16} e^{4\epsilon_0} \left(1 - \frac{r^2}{r_0^2} \right), \end{aligned}$$

showing that the law of depth reduces to Lamb's form, provided we take $h_0' = h_0 \cdot \frac{1}{16} e^{4\epsilon_0}$.

From these

$$\frac{\lambda^2 r_0^2}{g h_0'} = \kappa^2 / a.$$

Taking large values of a , we have from (19) for case (i),

$$\frac{\lambda^2 r_0^2}{g h_0'} = 4 \text{ or } 8. \quad (28)$$

The lower frequency corresponds to $j = 1, s = 2$ —a pair of nodal diameters in place of a pair of nodal hyperbolas. The higher frequency corresponds to $s = 0, j = 2$ —a nodal circle in place of a nodal ellipse.

Cases (ii) and (iv) are indistinguishable from one another in the limit, giving $\lambda^2 r_0^2 / g h_0' = 2$. This is the mode $s = 1, j = 1$, with a single nodal diameter.

Case (iii) gives $\lambda^2 r_0^2 / g h_0' = 6$ or 14. In the circular case, these arise from $j = 1, s = 3$ and $j = 2, s = 1$ respectively.

Case (vi) is interesting. From (26) we find in the limit that $\kappa^2 = 4a$, or $\lambda^2 r_0^2 / g h_0' = 4$. This case degenerates to the same form as the lower frequency of (28) with a pair of nodal diameters. These diameters are the limiting forms on the one hand of a pair of hyperbolas and on the other hand of the major and minor axes.

§ 8. Comparison with Longitudinal Oscillations.

The theories of *seiche* motions in lakes worked out by Chrystal* and Proudman† depend upon the assumption that the oscillations are purely longitudinal. It is of some interest, therefore, to work out the earlier frequencies for the basin of this paper on the longitudinal theory and to compare the results.

* 'Trans. Roy. Soc. Edin.,' vol. 41, Part 3, p. 599 (1905).

† 'Proc. Lond. Math. Soc.,' vol. 14, p. 240 (1915).

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If S be the area of the section of the lake normal to the length at a distance x from the origin and b be the breadth of the free surface there, the equation of the oscillations is*

$$\frac{g}{b} \frac{d}{dx} \left(S \frac{d\zeta}{dx} \right) + \lambda^2 \zeta = 0. \quad (29)$$

From (5) we find

$$b = \frac{2c}{\sqrt{a}} \left\{ a^2 - a - \frac{x^2}{c^2} (a - 1) \right\}^{1/2},$$

$$S = \frac{4ch_0}{3\sqrt{a}} \left\{ a^2 - a - \frac{x^2}{c^2} (a - 1) \right\}^{3/2}.$$

If we write

$$\beta = a^2 - a,$$

$$\gamma = (a - 1)/c^2,$$

equation (29) becomes

$$(\beta - \gamma x^2) \frac{d^2 \zeta}{dx^2} - 3\gamma x \frac{d\zeta}{dx} + \frac{3\lambda^2 \zeta}{2gh_0} = 0. \quad (30)$$

Assuming a solution $\Sigma A_n x^n$ in the vicinity of $x = 0$, we find the indices are 0, 1 and the relation is

$$A_{n+2} \beta(n+1)(n+2) = \left\{ \gamma n(n+2) - \frac{3\lambda^2}{2gh_0} \right\} A_n. \quad (31)$$

The series is not convergent at the point β/γ , or the extremity of the lake, unless it terminate. Hence we must have

$$\frac{3\lambda^2}{2gh_0} = \gamma n(n+2)$$

$$= n(n+2)(a-1)/c^2, \quad (32)$$

for some integral value of n .

The lowest mode is obtained by putting $n = 1$.

Then $\lambda^2 c^2 / gh_0 = 2(a-1)$, exactly as in (21). This result might have been anticipated as, since

$$\zeta \propto \cosh \xi \cos \eta$$

$$\propto x,$$

the transverse velocity, which is proportional to $\partial \zeta / \partial y$, is zero.

For $n = 2$, a two-noded vibration, (32) gives

$$\lambda^2 c^2 / gh_0 = \frac{16}{3} (a-1). \quad (33)$$

* Lamb, "Hydrodynamics," p. 267.

The corresponding result is the smaller value in (19). If we assume $a - 1 = \delta$ = a small quantity, (19) gives

$$\begin{aligned}\frac{\lambda^2 c^2}{gh_0} &= 6a - 3 - 2\sqrt{a^2 - a + \frac{1}{4}} \\ &= \frac{1}{3}\delta + O(\delta^2).\end{aligned}$$

This exhibits the effect of the departure from purely longitudinal motion in a narrow lake of this type.

Similarly, taking the three-noded vibration we have from (32)

$$\frac{\lambda^2 c^2}{gh_0} = 10(a - 1) = 10\delta.$$

The corresponding result (22) gives

$$\begin{aligned}\frac{\lambda^2 c^2}{gh_0} &= 10a - 7 - 4\sqrt{a^2 - 2a + \frac{25}{16}} \\ &= 10\delta + O(\delta^2).\end{aligned}$$

The Direction of Magnetisation of Single Ferromagnetic Crystals.

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§ 1. *Introduction.*

The study of the magnetisation of single crystals of ferromagnetic substances has shown that there are definite relations between magnetic properties and crystalline structure. One of the most important, the relation between the crystalline structure and the direction of magnetisation, will be studied in this paper. It is well known that on applying a magnetic field to a crystal the direction of the magnetisation produced does not, in general, coincide with that of the field (here and elsewhere, unless the external field is specifically mentioned, the effective field is to be understood). The phenomenon has been extensively studied experimentally, but hitherto there has been no entirely satisfactory theory.

A theory, at least partially successful, was proposed by Mahajani,* who assumed that the elementary magnets are electron orbits. Owing to their

* G. S. Mahajani, 'Phil. Trans.,' A, vol. 228, p. 63 (1929).

magnetic interaction, these magnets possess a mutual potential energy which in general depends upon their orientation, and hence leads to deviations between the directions of magnetisation and field. In the case of non-cubic crystals, it is sufficient to consider the elementary magnets as simple dipoles, but in the case of cubic crystals, the dipole energy is independent of the orientation of the dipoles, and it becomes necessary to consider the quadrupole moments. Mahajani showed that this theory accounts qualitatively for the various effects observed in iron (with a cubic structure) and pyrrhotite (with a non-cubic structure).

To this theory two objections may be raised. In the first place, Mahajani did not attempt to deal quantitatively with the effect in non-cubic crystals. Rough calculations have now been made for cobalt, which has a hexagonal close-packed lattice, and it is found that the magnitude of the effect, according to Mahajani's theory, is much smaller than that observed. Secondly, it is now known that the elementary magnets originate not in electron orbits, but in electron spins, and presumably have no quadrupole moments; Mahajani's theory thus fails completely in the case of cubic crystals.

In this paper it is suggested that the facts may be explained by taking into account the magnetic interaction between each electron and the atom to which it belongs; such interaction is known to exist, and gives rise to multiplet separation. We suppose that this interaction can be represented by a field G , fixed in the crystal, which we call the *crystalline field*. It is assumed that G can lie in a number of possible directions which bear simple relations to the crystal structure, corresponding to various orientations of the atoms.

The theory has been worked out only for cases when the applied field is great enough to produce saturation and when thermal effects can be neglected. Thus, strictly, the theory applies only to zero temperature; it may, however, be applied as an approximation to ordinary room temperatures. It is found that by means of the crystalline field the deviation between the directions of the applied field and the magnetisation can be satisfactorily explained in both cubic and non-cubic crystals, and that the required magnitude of the field is in agreement with that deduced from spectroscopic data. It is hoped later to investigate other effects of the crystalline field on magnetic phenomena. There is no reason to suppose that the crystalline field exists only in ferromagnetic crystals, and it may prove possible to develop a theory of paramagnetic crystals at low temperatures on the lines of the theory of Foëx,* according to which there are departures from the Weiss law for

* G. Foëx, 'Ann. Physique,' vol. 16, p. 174 (1921).

the susceptibility. A similar investigation on ferromagnetic crystals might help to elucidate the problem of the failure of the Weiss law just above the Curie point.

§ 2. *Effect of Crystalline Field.*

We have to calculate the magnetisation at zero temperature of a crystal consisting of $2n$ atoms, each possessing y effective electrons, taking into account the exchange interaction of the electrons, the applied magnetic field $\mathbf{H}$, and the crystalline field $\mathbf{G}$. $\mathbf{G}$ varies from atom to atom, and it is assumed that the atoms may be divided into p equal groups $a, b, \dots$ with the corresponding values $G_a, G_b, \dots$ for $\mathbf{G}$, the magnitude G being assumed constant.

The energy arising from the exchange interaction is given by*

$$E = -\frac{1}{2} \sum_{r>s} J_{rs} \{1 + (\boldsymbol{\sigma}_r, \boldsymbol{\sigma}_s)\},$$

where $\boldsymbol{\sigma}_r, \boldsymbol{\sigma}_s$ are the spin vectors of the r th and s th electrons, and J_{rs} is their exchange energy. When magnetic fields are absent, s , the resultant spin of the electrons, is a constant of the motion, and the mean energy $\bar{E}$ of the stationary states of the system with the eigen-value s is given by†

$$\bar{E} = -\frac{zJ_0}{2n} s^2 + \text{const.},$$

where z is the number of "nearest neighbours" of any atom. It is here assumed that the exchange interactions between electrons belonging to the same atom are much greater than those between electrons belonging to different atoms; and further, that the exchange energy corresponding to a simple transposition of a pair of electrons belonging to neighbouring atoms has the same value J_0 for all such pairs, and is negligible for pairs of electrons belonging to atoms which are not closest neighbours. The validity of these assumptions will be discussed later. When the magnetisation is nearly saturated, the mean square deviation $\overline{\Delta E^2}$ of the energy from its mean value $\bar{E}$ is small, and hence the eigen-values of E are approximately the same as those of $\bar{E}$. We may therefore replace E by $\bar{E}$. Assuming that this remains true when magnetic fields are present, the energy of the system is

$$E = -\frac{zJ_0}{2n} s^2 - \sum_{a,b,\dots} \mu_B (\mathbf{H} + \mathbf{G}_a, \sum_a \boldsymbol{\sigma});$$

* See P. A. M. Dirac, 'Proc. Roy. Soc.,' A, vol. 123, p. 714 (1929).

† W. Heisenberg, "Probleme der modernen Physik," Hirzel, Leipzig, p. 114; F. C. Powell, 'Phys. Soc. Proc.,' vol. 42, p. 390 (1930).

μ_B denoting a Bohr magneton. The problem is to find the magnetisation in the stationary state of lowest energy.

Now in dealing with many electrons, we may treat the variables which describe the whole system classically. For example, in Heisenberg's* treatment of ferromagnetism, the partition function remains unaltered (to the highest order in n) if we replace the double summation, over integral values of s and its component m , by a double integration over continuous values; the quantum and classical partition functions differ only because the statistical weights are different. We therefore replace the quantum variable $\sum_a \sigma$ by the classical vector $(2yn/p) \cdot \zeta_a$, and s by $(yn/p) \sum_{a,b,\dots} \zeta_a$.

The energy becomes

$$E = -\frac{zJ_0}{2n} \cdot \left(\frac{yn}{p}\right)^2 \left(\sum_{a,b,\dots} \zeta_a\right)^2 - 2\mu_B \left(\frac{yn}{p}\right) \cdot \sum_{a,b,\dots} (H + G_a, \zeta_a).$$

E must be a minimum for arbitrary variations of the vectors ζ_a , etc. First consider variations which are subject to

$$\zeta_a = \text{const.}, \quad \zeta_b = \text{const.}, \quad \text{etc.};$$

the usual method gives the conditions

$$-\frac{zJ_0}{2n} \cdot \left(\frac{yn}{p}\right)^2 \cdot \sum_{a,b,\dots} \zeta_a - \mu_B \cdot \frac{yn}{p} \cdot (H + G_a) + \lambda_a \zeta_a = 0, \text{ etc.},$$

λ_a , etc., being constants. These conditions may be written

$$\zeta_a = \frac{N\zeta + H + G_a}{[N\zeta + H + G_a]}, \text{ etc.}, \quad (1)$$

where

$$\zeta = \frac{1}{p} \sum_{a,b,\dots} \zeta_a$$

and

$$N = \frac{yzJ_0}{2\mu_B} = \frac{3kT_c \dagger}{(y+2)\mu_B},$$

T_c being the Curie temperature. If N is positive and large compared with G and H , each of the constants $\lambda_a, \dots$ is positive. Now make arbitrary variations $\delta\zeta_a$, etc. The variation in E is, using the above conditions,

$$\delta E = -2 \sum \lambda_a (\zeta_a, \delta\zeta_a) = -\sum \lambda_a \delta\zeta_a^2.$$

* 'Z. Physik,' vol. 49, p. 619 (1928).

† See F. C. Powell, *loc. cit.*

If E is a minimum, $\delta E \geq 0$ for all variations, so that the magnitude of each ζ_a must take its maximum value, which is 1. These conditions, together with conditions (1), are equivalent to the statement that each group of atoms is fully magnetised in the direction of the resultant of H , G , and a field $N\zeta$ which is just the molecular field of Weiss.

By summation of equations (1), we obtain an equation to determine ζ :

$$\zeta = \frac{1}{p} \sum_{a,b} \frac{N\zeta + H + G_a}{|N\zeta + H + G_a|}. \quad (2)$$

The resultant magnetisation of the crystal is equal to $2\pi n\mu_B\zeta$. The evaluation of ζ is essentially different in the cases of cubic and non-cubic crystals.

§ 3. Cubic Crystals.

In order to evaluate the right-hand side of (2), we write

$$\frac{N\zeta + H + G_a}{|N\zeta + H + G_a|} = \frac{\alpha + G_a}{|\alpha + G_a|} = (\alpha + G_a) \{\alpha^2 + 2(\alpha, G_a) + G^2\}^{-1/2}, \quad (3)$$

where α is written for $N\zeta + H$, and expand in powers of G , the assumption being made that G/N is small.

Taking axes of reference along the cubic axes, we now suppose that G can take up the orientation (p, q, r) . The symmetry of the crystal requires that G can also take up any of the 48 orientations

$$(\pm p \pm q \pm r), \quad (\pm q \pm r \pm p), \quad \text{etc.}$$

Each term in the expansion of the right-hand side of (3) must then be averaged over these 48 directions. We find

$$\zeta_x = \left[\frac{1}{48} \sum_a \frac{\alpha + G_a}{|\alpha + G_a|} \right]_x = \frac{\alpha_x}{\alpha} \left\{ 1 - \frac{1}{3} \frac{G^2}{N^2} + O(G^4) \right\} + \gamma \left(\frac{\alpha_x}{\alpha} \right)^3, \quad (4)$$

where

$$\gamma = \frac{5}{2} \cdot \frac{G^4}{N^4} \left(\frac{1}{2} - \frac{5}{8} (p^4 + q^4 + r^4) \right). \quad (5)$$

To a sufficient approximation it follows that

$$\zeta = 1 - G^2/3N^2. \quad (6)$$

Denoting the vector $(\gamma\zeta_x^3, \gamma\zeta_y^3, \gamma\zeta_z^3)$ by β , (4) may be written

$$\zeta_x = \frac{\alpha_x}{\alpha} \{1 + O(G^2)\} + \beta_x,$$

(assuming γ small). Thus $\zeta - \beta$ is parallel to α , and therefore to $\zeta + H/N$. But $\zeta \gg H/N$, so that $H/N + \beta$ is parallel to ζ , or

$$\frac{H_x}{\zeta_x} + \gamma N \zeta_x^2 = \frac{H_y}{\zeta_y} + \gamma N \zeta_y^2 = \frac{H_z}{\zeta_z} + \gamma N \zeta_z^2. \quad (7)$$

Equation (6) shows that the saturation value of the magnetisation is reduced, while (7) shows that the direction of magnetisation does not coincide with that of the applied field. When $\gamma > 0$, the deviation of the direction of magnetisation from that of the applied field is always *towards* the nearest cubic axis; when $\gamma < 0$, the deviation is *away from* the nearest cubic axis. The deviation vanishes in the direction of the [100], [110] and [111] axes.

It is interesting to compare equations (7) with those obtained when one assumes that the crystal possesses an energy

$$c(\zeta_y^2 \zeta_z^2 + \zeta_x^2 \zeta_y^2 + \zeta_x^2 \zeta_z^2), \quad (8)$$

in addition to the energy in the applied field (an energy term of this form is obtained when the elementary magnets possess quadrupole moments). We have

$$E = -2yn\mu_B(H, \zeta) + c(\zeta_y^2 \zeta_x^2 + \zeta_x^2 \zeta_z^2 + \zeta_z^2 \zeta_y^2).$$

The conditions for a stationary value of E , subject to

$$\zeta = 1,$$

are

$$-yn\mu_B H_x + c\zeta_x(\zeta_y^2 + \zeta_z^2) + \lambda\zeta_x = 0, \text{ etc.,}$$

where λ is a constant, whence

$$\frac{H_x}{\zeta_x} + \frac{c}{yn\mu_B} \zeta_x^2 = \frac{H_y}{\zeta_y} + \frac{c}{yn\mu_B} \zeta_y^2 = \frac{H_z}{\zeta_z} + \frac{c}{yn\mu_B} \zeta_z^2.$$

These equations are identical with equations (7), provided $c = yn\mu_B N\gamma$. The direction of magnetisation when a crystalline field is present is therefore the same as if the crystal possesses an additional energy of the form (8).

§ 4. Iron and Nickel.

This section is devoted to a comparison of the above results with the experimental data for iron (body-centred cubic) and nickel (face-centred cubic), the magnetic properties of which have been investigated very completely by several workers.* We thus obtain an estimate of the magnitude of the crystalline field.

* Iron: Beck, 'Dissertation,' Zürich (1918); Webster, 'Proc. Roy. Soc.,' A, vol. 107, p. 496 (1925); Honda and Kaya, 'Sci. Rep. Tôhoku,' vol. 15, p. 721 (1926), and others. Nickel: Sucksmith, Potter and Broadway, 'Proc. Roy. Soc.,' A, vol. 117, p. 471 (1928); S. Kaya, 'Sci. Rep. Tôhoku,' vol. 17, p. 639 (1928).

Nickel.—We shall use here the results of Kaya (*loc. cit.*) who measured the components of magnetisation parallel and perpendicular to the external field in three oblate spheroids whose equatorial planes coincided respectively with the principal planes (100), (110), (111), the field lying in the equatorial plane. Measurements were made for both saturated and non-saturated states, but we are here concerned only with the former. From these measurements one can calculate (i) the magnitude of the resultant intensity in any direction, and (ii) the angular deviation between the directions of the resultant intensity and the effective field.

Kaya found that the magnitude of the resultant intensity was equal in all directions (within 2 per cent.) to the constant value 503 at 20° C. The direction of magnetisation in the three principal planes will now be considered.

(100) *Plane*.—Suppose the directions of the effective field and resultant intensity make angles ϕ , ψ respectively with a tetragonal axis. Writing $(H_x, H_y, H_z) = H (\cos \phi, \sin \phi, 0)$; $(\zeta_x, \zeta_y, \zeta_z) = (\cos \psi, \sin \psi, 0)$, equations (7) lead to the relation

$$\sin (\phi - \psi) = \gamma N / 4H \sin 4\psi.$$

For a constant field H , $\sin (\phi - \psi)$ is therefore a periodic function of ψ with period $\frac{1}{2}\pi$. This is borne out by Kaya's measurements.

Further, the amplitude of $\sin (\phi - \psi)$ is given by

$$\sin (\phi - \psi)_{\max.} = |\gamma N / 4H|,$$

and hence $H \sin (\phi - \psi)_{\max.}$ should be constant. This also is in agreement with the experimental data, as is shown by the following table.

$H_{\text{eff.}}$	$\sin (\phi - \psi)_{\max.}$	$H \sin (\phi - \psi)_{\max.}$
408.5	0.0572	23.4
501.0	0.0470	24.0
595.0	0.0398	23.6

Taking 23.7 as the average value of $H \sin (\phi - \psi)_{\max.}$, we obtain for γN

$$\gamma N = -94.8$$

(the negative sign means that the deviation of the direction of the resultant intensity from that of the field is always away from the nearest cubic axis).

(110) *Plane*.—This is the most interesting of the planes, as it contains all

three principal axes. As before, we measure ϕ , ψ from a tetragonal axis, and writing

$$(H_x, H_y, H_z) = H \left(\cos \phi, \frac{1}{\sqrt{2}} \sin \phi, \frac{1}{\sqrt{2}} \sin \phi \right);$$

$$(\zeta_x, \zeta_y, \zeta_z) = \left(\cos \psi, \frac{1}{\sqrt{2}} \sin \psi, \frac{1}{\sqrt{2}} \sin \psi \right)$$

obtain from equations (7) the relation

$$\sin(\phi - \psi) = \gamma N / 8H \cdot \sin 2\psi (3 \cos 2\psi + 1).$$

A comparison of the theoretical and experimental relations between ϕ and ψ is made in fig. 1. The experimental curve corresponds to an effective field of 296.3 gauss, and the theoretical curve is drawn for γN equal to -94.8 (the value which was found for the (100) plane). The agreement is satisfactory. In making comparisons between theoretical and experimental results, it must be remembered that the theory itself is not exact, as we have neglected all but lowest powers of G in applying equation (2), and the errors in our approximate formulæ for the deviation $(\phi - \psi)$ may easily amount to as much as 10 per cent. of the maximum deviation under the same field in the (110) plane.

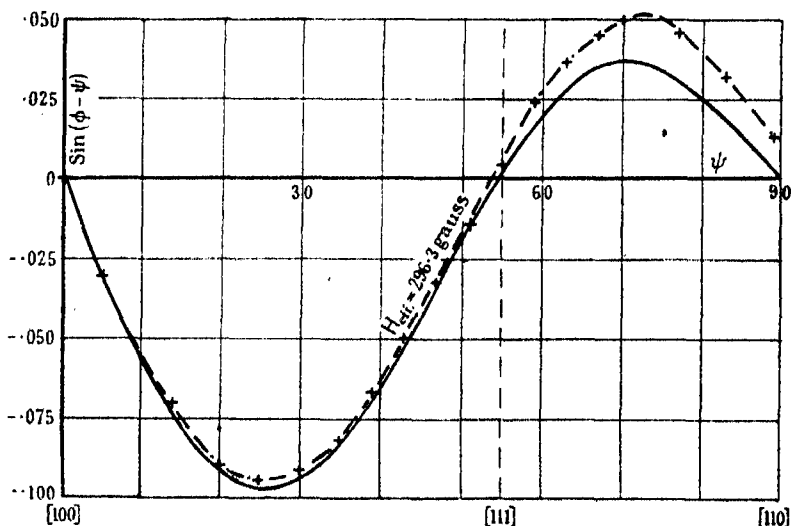


FIG. 1.—Direction of Magnetisation in (110) plane in Nickel. —, theoretical curve; — — —, experimental curve.

(111) Plane.—It is clear from equations (7) that if H lies in the plane, the resultant intensity does not. The demagnetising effect therefore modifies

not only the magnitude, but also the direction of the effective field. In this case a more elaborate treatment is necessary, the simplest being that adopted by Mahajani (*loc. cit.*) which regards the demagnetising force as constraining the resultant intensity to lie in the plane. The energy must then be made stationary, subject to the additional condition

$$\zeta_x + \zeta_y + \zeta_z = 0.$$

It is then found that there is no deviation between the directions of the effective field and the resultant intensity.

Kaya actually found a periodic deviation with period 60° , but the amplitude was very small, being less than 4 per cent. of the maximum deviation under the same field in the (110) plane, and for the reasons stated above, differences of this magnitude between experiment and theory are not serious.

Iron.—The experimental results for iron are similar to those for nickel, and the agreement with theory is equally satisfactory. A detailed examination has already been made by Mahajani. There is one important difference between the two cases; whereas in nickel the deviation of the magnetisation from the direction of the field is always away from the nearest cubic axis, in iron the deviation is always towards the nearest cubic axis. This results in γ_N having opposite signs in the two cases. Using the results of Honda and Kaya (*loc. cit.*) we find

$$\gamma_N = + 313.$$

Magnitude of Crystalline Field.—The magnitude G may now be roughly estimated from equation (5), assuming values for (p, q, r) . The most likely values for the orientation (p, q, r) are:—

$$(1, 0, 0), \quad \text{giving} \quad \gamma = -\frac{5}{6} \cdot \frac{G^4}{N^4},$$

$$(1/\sqrt{2}, 1/\sqrt{2}, 0), \quad \text{giving} \quad \gamma = +\frac{5}{24} \cdot \frac{G^4}{N^4},$$

$$(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}), \quad \text{giving} \quad \gamma = +\frac{5}{9} \cdot \frac{G^4}{N^4}.$$

For nickel, $\gamma < 0$, making the orientation $(1, 0, 0)$ appear probable. Taking $y = 1$, $T_c = 645^\circ \text{ K.}$, we then obtain for G

$$G = 5.6 \times 10^6 \text{ gauss.}$$

For comparison, the molecular field which is equivalent to the exchange interaction is

$$N = 9.6 \times 10^6 \text{ gauss.}$$

For iron, $\gamma > 0$, and it is not clear which orientation ought to be taken. Taking the orientation $(1/\sqrt{2}, 1/\sqrt{2}, 0)$, $y = 3$, $T_c = 1047^\circ \text{ K.}$ we obtain

$$G = 1.05 \times 10^6 \text{ gauss};$$

taking the orientation $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$, we obtain

$$G = 8.2 \times 10^5 \text{ gauss};$$

and for comparison,

$$N = 9.3 \times 10^6 \text{ gauss.}$$

It is convenient to discuss here the various assumptions which have been made in the course of the calculations. In § 3 it was assumed, purely for convenience in the mathematics, that G/N is small. This assumption is consistent with the above numerical values, from which G/N is seen to be about $1/10$.

In § 2 we made the assumption, upon which Heisenberg's treatment of a ferromagnetic substance possessing more than one effective electron per atom rests entirely, that the exchange interaction between electrons in the same atom is much greater than that between electrons in different atoms. The exchange interactions between the electrons of an atom give the energy separations between different multiplet states arising from the same orbits, and these separations are assumed large in order that all the atoms may remain in the same l, s state. In order to justify the assumption we must know the energy levels of an atom in a crystal, but, in the absence of these data, we may perhaps use the data relating to single atoms which are obtained from spectroscopic measurements. Consider, for example, iron, the lowest levels of which are given below, the term values being counted upwards from the lowest known level.

Terms of Fe (H. N. Russell).*

Type	⁵ D.	⁵ F.	³ F.
Term	0—978	6928—8155	11976—12969

We may neglect all but the ⁵D states provided that the energy difference between the ground state and the lowest ⁵F state is large compared with kT_c , or $ch\Delta\nu/kT_c$ is large compared with 1. Taking $\Delta\nu$ equal to 6928, we obtain for $ch\Delta\nu/kT_c$ the value 9.5. In a crystal the electron orbits will be con-

* 'Astrophys. J.,' vol. 68, p. 151 (1928).

siderably modified, so that the actual numerical term values above are of no significance; nevertheless, the above and similar data for Fe^+ , cobalt, and nickel show that the separations between different multiplets are usually sufficiently large to allow the neglect of all but the lowest multiplet, and it seems reasonable to suppose that this is the case for atoms in crystals of iron, cobalt and nickel.

Finally, we have supposed that the crystalline field G represents the (ls) interactions of the atoms in the crystal. We must investigate whether this interaction can account for fields of the magnitude we require. For Fe , the separation Δv between the terms ${}^5D_4$ and ${}^5D_0$ is 978 wave-numbers, indicating the presence of a field of $ch\Delta v/8\mu_B$ gauss, or roughly 2×10^6 gauss, which is about twice as large as the field we require. The (ls) interaction is therefore adequate to account for the crystalline field. It is not surprising to find that the (ls) interactions are smaller for atoms in a crystal than for single atoms, since the outer orbits will be increased in size (owing to the presence of neighbouring centres of force) and the (ls) interactions correspondingly decreased.

§ 5. Non-Cubic Crystals.

In order to evaluate the right-hand side of (2) for non-cubic crystals, we adopt the same procedure as in the case of cubic crystals, expanding the summand in powers of G . Assuming that G can take up the orientations $\pm (p_a, q_a, r_a)$, $\pm (p_b, q_b, r_b)$, etc., we find that

$$\zeta_x = \frac{\alpha_x}{\alpha} \left\{ 1 - \frac{1}{2} \frac{G^2}{N^2} + \frac{3}{2} \frac{G^4}{N^4} (P\alpha_x^2 + Q\alpha_y^2 + R\alpha_z^2) \right\} - \frac{G^2}{N^2} \frac{P\alpha_x}{\alpha} + O(G^4), \text{ etc.},$$

where $\alpha = N\zeta + H$, and $P = \bar{p}^2 = \text{average value of } p_a^2, p_b^2, \dots$; $Q = \bar{q}^2$; $R = \bar{r}^2$.

Denoting the vector

$$\left(\frac{G^2}{N^2} \cdot \frac{P\alpha_x}{\alpha}, \quad \frac{G^2}{N^2} \cdot \frac{Q\alpha_y}{\alpha}, \quad \frac{G^2}{N^2} \cdot \frac{R\alpha_z}{\alpha} \right)$$

by β , we see that $\zeta + \beta$ is parallel to α , and therefore to $\zeta + H/N$, so that $H/N - \beta$ is parallel to ζ , or

$$\frac{H_x}{\zeta_x} - \frac{G^2}{N} \cdot P = \frac{H_y}{\zeta_y} - \frac{G^2}{N} \cdot Q = \frac{H_z}{\zeta_z} - \frac{G^2}{N} \cdot R. \quad (9)$$

These equations may be compared with those obtained when one assumes a molecular field

$$((N + N_1) \zeta_x, (N + N_2) \zeta_y, (N + N_3) \zeta_z).$$

They are

$$\frac{H_x + N_1 \zeta_x}{\zeta_x} = \frac{H_y + N_2 \zeta_y}{\zeta_y} = \frac{H_z + N_3 \zeta_z}{\zeta_z}, \quad (10)$$

which are identical with equations (9) provided

$$N_1 = -\frac{G^2 P}{N}, \text{ etc.}$$

Thus the effect of the crystalline field is precisely the same as the effect of the additional molecular field ($N_1 \zeta_x$, $N_2 \zeta_y$, $N_3 \zeta_z$) which Weiss postulated in order to explain the deviation between the directions of the field and the magnetisation in pyrrhotite.

Dipole Energy.—In dealing with non-cubic structures, the dipole energy must also be taken into account, since it is dependent upon the orientation of the magnetisation. The question arises whether the ordinary classical methods of calculating the dipole energy of a system of electrons remains valid in the quantum theory. In a stationary state of the system, the resultant spin s has a definite numerical value, but it is not in general true to say that the spins of the electrons set themselves parallel or antiparallel to the field; one cannot give any meaning to the direction of spin of an individual electron. But it may be proved that in the particular case $s = \gamma n$, all spins must be parallel to some direction, and may then be treated as parallel vectors. Thus when the magnetisation is saturated, the classical method of treatment remains valid. One ought, of course, to treat an electron not as a dipole situated at a lattice point, but as a Schrödinger distribution of dipoles. But when an electron is in an S-state, it is exactly equivalent to a dipole at the lattice point, and probably no serious error is introduced in making this simplification in every case.

Now consider a system of $2n$ dipoles, each of strength $\gamma \mu_B$, oriented in the direction ζ . The dipole energy of the system is of second degree in ζ_x , ζ_y , ζ_z , and by suitable choice of axes can always be reduced to the form

$$E_d = -\gamma n \mu_B (F_x \zeta_x^2 + F_y \zeta_y^2 + F_z \zeta_z^2).$$

When there is cubic symmetry, F_x , F_y , and F_z are equal and E_d is independent of the orientation, a result which was tacitly assumed in treating cubic crystals.

The average force at a lattice point due to the dipoles at the remaining lattice points is ($F_x \zeta_x$, $F_y \zeta_y$, $F_z \zeta_z$), so that the effect of dipole interaction is the same as that of an additional molecular field ($F_x \zeta_x$, $F_y \zeta_y$, $F_z \zeta_z$).

Dipole interaction and the crystalline field are together equivalent to an additional molecular field ($N_1\zeta_x, N_2\zeta_y, N_3\zeta_z$), with

$$N_1 = F_x - G^2P/N; \quad N_2 = F_y - G^2Q/N; \quad N_3 = F_z - G^2R/N. \quad (11)$$

§ 6. Cobalt.

In this section it will be shown that equations (10) and (11) are adequate to account for the phenomena observed in cobalt. A comparison of equations (10) with the experimental magnetisation curves enables N_1, N_2, N_3 to be determined. The quantities F_x, F_y, F_z are then calculated, and an estimate of G obtained from equation (11).

At room temperatures, cobalt has a hexagonal close-packed lattice. Kaya* measured the magnetisation in two circular discs cut in the principal planes† (0001) and (10 $\bar{1}$ 0). [0001] was found to be an axis of easy magnetisation, (0001) a plane of difficult magnetisation. The saturation intensity was 1422 at 26° C.

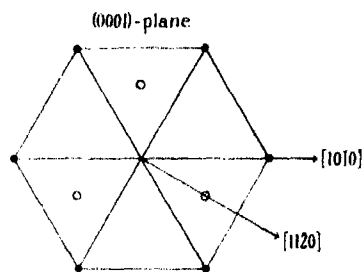


FIG. 2.—The Hexagonal Close-packed Lattice.

Taking [0001] as the z-axis, we have at once, from consideration of symmetry, that N_1 is equal to N_2 .

(10 $\bar{1}$ 0) Plane.—Let H act in the plane of the disc, and suppose H, ζ make angles ϕ, ψ with the axis [0001]. Equations (10) then give

$$H \sin(\phi - \psi) = (N_3 - N_1) \sin \psi \cos \psi.$$

A comparison is made with the experimental curve in fig. 3. The theoretical curve is drawn with $N_3 - N_1$ equal to 6.8×10^3 ; the experimental curve corresponds to a constant effective field of 9016 gauss. The lag of the experimental curve behind the theoretical curve is probably due to hysteresis.

(0001) Plane.—Since N_1 is equal to N_2 , the deviation $\phi - \psi$ ought to vanish. This is in agreement with the experiments of Kaya, who found that the component of magnetisation perpendicular to the field was so small that no regular variation could be observed.

* 'Sci. Rep. Tôhoku,' vol. 17, p. 1157 (1928).

† The base plane of the hexagonal lattice is expressed by (0001), a face of the hexagonal prism by (10 $\bar{1}$ 0). (0001) and (10 $\bar{1}$ 0) intersect in the axis [10 $\bar{1}$ 0], and have normals [0001] and [11 $\bar{2}$ 0] respectively, v. fig. 2.

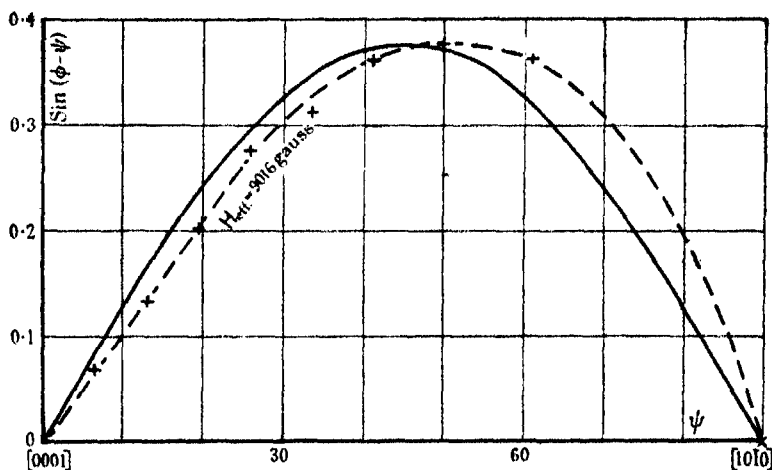


FIG. 3.—Direction of Magnetisation in (1010) plane in Cobalt. —, theoretical curve. ---, experimental curve.

The phenomena are accounted for completely by means of a molecular field with

$$N_1 = N_2; N_3 - N_1 = 6.8 \times 10^3.$$

Magnitude of Crystalline Field.—It is first necessary to calculate F_x , F_y , and F_z . F_x , it will be remembered, is the x -component of the field at a lattice point due to the dipoles at the remaining lattice points, these dipoles being orientated in the direction of the x -axis.

Now if U is the magnetic potential due to unit poles placed at the lattice points, then

$$F_x = y\mu_B \frac{\partial^2 U}{\partial x^2}, \text{ etc.}$$

and therefore

$$F_x + F_y + F_z = 0.$$

In the case of cobalt, we have further

$$F_x = F_y.$$

It is therefore necessary to calculate only one of the three quantities F_x , F_y , F_z . The others may be found by using the last two equations.

Referring to fig. 4, the sides of the unit cell in the lattice of cobalt are*

$$a = 2.514 \times 10^{-8} \text{ cm.}$$

$$c = 4.105 \times 10^{-8} \text{ cm.}$$

* Int. Crit. Tables (1926).

We have attempted to estimate F_z roughly by direct summation for all atoms within distance $3a$ or less (this includes about 160 atoms). Taking dipoles of unit strength, the component along Oz of the field at a lattice point is found to be 4.2×10^{21} gauss. For dipoles of strength $2\mu_B$, the force is given by

$$F_z = 77 \text{ gauss,}$$

so that $F_z = F_y = -38$ gauss. The dipole interaction is therefore equivalent to an additional molecular field with

$$N_3 - N_1 = F_z - F_x = 10^2 \text{ gauss, roughly.}$$

This is only $1/68$ the field required in order to account for Kaya's results. The estimate of F_z is, of course, very rough, and may be in considerable error. But it seems quite certain that dipole interaction can account for only a small fraction of the additional molecular field.

We can now estimate the order of magnitude G . Taking $y = 2$, $T_c = 1404^\circ \text{K.}$, we obtain from equations (11)

$$P = Q; (P - R) G^2 = 1.03 \times 10^{11}.$$

$(P - R)$ is greatest when R vanishes (*i.e.*, when G lies in the (0001) plane); the value of $P - R$ is then $1/2$. G must therefore be at least 4.5×10^5 gauss; roughly speaking, G is of the order of 10^6 gauss. We have already found that (ls) interaction is adequate to account for fields of this magnitude.

Thus the observed deviation between the direction of magnetisation of a single crystal of iron, cobalt, or nickel and the direction of the applied field can be accounted for by taking into account the magnetic interaction between the effective electrons (*i.e.*, the electrons whose magnetic moments contribute to the magnetisation of the crystal) and the atoms to which they belong.

I wish to express my thanks to Mr. R. H. Fowler for suggesting this investigation, and for his interest and encouragement during its progress.

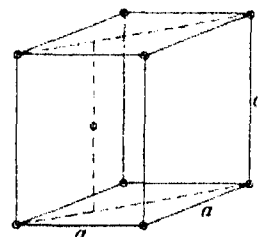


FIG. 4.—The Unit Cell of Cobalt.

*Energy Losses of Electrons in Carbon Monoxide and
Carbon Dioxide.*

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(Communicated by O. W. Richardson, F.R.S.—Received September 15, 1930.)

Introduction.

In a previous paper published in these 'Proceedings'* a report was given of some measurements on the energy losses suffered by electrons in nitrogen at pressures sufficiently low to ensure that practically only single collisions would take place. Electrons of homogeneous speed drawn from a hot cathode were fired through the gas and the velocity distribution in the emergent beam subsequently analysed by a combination of one longitudinal and one transversal electric field, the latter of a kind which would give refocussing of a slightly divergent incident beam at the entrance slit of the electron detector.† The two most prominent characteristic energy losses observed in nitrogen were shown to be associated with energy levels known from the absorption spectrum of the nitrogen molecule in the far ultra-violet. The present investigation is an extension of this work to the two gases carbon monoxide and carbon dioxide. The former of these two was chosen as a typical diatomic gas, the energy levels of which are now fairly well known through the work of several investigators in recent years. Carbon dioxide was studied in addition to this, in view of the possibility that traces of this gas could have been formed from the carbon monoxide in contact with the hot cathode in the experiments with the latter gas. The experimental arrangements remained essentially the same as in the case of nitrogen. The tube was the one described in the previous paper referred to. The primary slit S_1 of sheet copper, which had been contaminated by mercury in the meantime when the tube was left standing without cooling the traps, was now replaced by a similar slit made of sheet silver. The cathode was coated with a mixture of barium and strontium oxides. As in the case of nitrogen all measurements were made with the gas continuously flowing through the apparatus, the pressure readings referring to the conditions in the tube through which the gas was admitted to the collision space.

* Rudberg, 'Proc. Roy. Soc.,' A, vol. 129, p. 628 (1930).

† Hughes and Rojansky, 'Phys. Rev.,' vol. 34, p. 284 (1929); Hughes and McMillen, *ibid.*, vol. 34, p. 291 (1929).

Carbon Monoxide.

Carbon monoxide was prepared from sodium formate and concentrated sulphuric acid.* A sufficient amount of pure formate was contained in an evacuated bulb connected to the pump through an all-glass line comprising a tube with caustic potash, wash bottles with concentrated sulphuric acid and a large storage flask, permanently attached to a phosphor-pentoxide tube. After evacuation sulphuric acid was slowly admitted and the whole system washed repeatedly with the gas formed before the product was stored. Before being admitted to the collision apparatus through the capillary leak, the gas was dried further by passing it through two more phosphor-pentoxide tubes. The pressures used ranged from 7×10^{-3} to 62×10^{-3} mm. in different experiments. The dull-emitting cathode layer was found to be very stable in the presence of this gas, much more so, in fact, than in the case of nitrogen. Consequently the thermionic emission could be kept very constant in the course of a run. Blank tests were measured as usual to distinguish maxima due to inelastic scattering from the electrodes from the effects of collisions in the gas. All measurements included in the following table were obtained using the method of varying the retarding electric field with the deflecting voltage kept constant, as previously described.

Some typical curves are shown in fig. 1. All the curves obtained with this gas are remarkably steady, the general appearance as well as almost all the details being rather well reproducible in the different runs using different pressures and voltages. It is true that the bombarding voltage has not been varied between such wide limits in the present experiments as in the work on nitrogen, but a glance at Table I of the present paper will show that the position of the maxima is independent of the primary voltage also in the present case. In this work the voltage was mostly so chosen as to yield a suitable current to the electron collector and at the same time a good resolving power. The energy values (in volts) corresponding to the several maxima in the distribution curves are listed in Table I, together with the values of pressure and voltage in each case. The total emission from the hot cathode, kept constant during the whole time that a series of readings is being taken, was 35.6×10^{-5} amps. for all measurements included in this table.

The most conspicuous feature of the curves obtained from the blank runs is the maximum near 6.5 volts. In the curves with gas present in the tube this maximum often exhibits a remarkable change in relative intensity from

* Guye, *Stählers Handb. Arbeitsmethoden anorg. Chem.*, vol. 4, p. 89 (1926).

one series to the other, which is not directly related to differences in bombarding voltage or gas pressure, but rather suggests that the appearance of this maximum depends, at least to some extent, on the relative position of the cathode

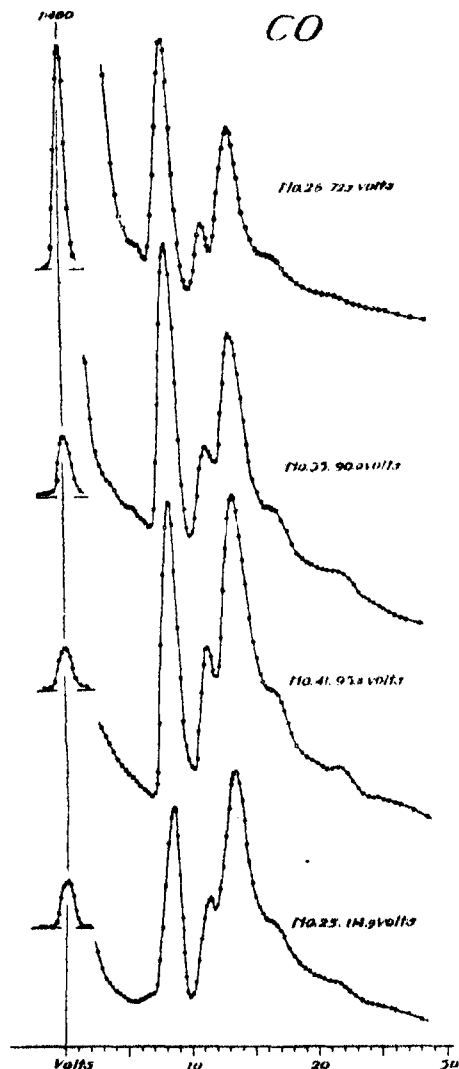


FIG. 1.

with respect to the perforated platinum screen and entrance slit S_1 . This maximum, therefore, is not to any appreciable extent due to collisions of the electrons with molecules of the gas. The first maximum at 5.3 volts has only been observed in comparatively few cases. The corresponding runs were

Table I.—Carbon Monoxide. Current 35.6×10^{-5} amps.

No.	Voltage.	$\frac{p}{\times 10^{-3}}$	V_1	V_2	V_3	V_4	V_5	V_6	V_7
32	59.8	40.3	—	6.50	8.30	11.30	13.80	16.70	—
26	72.7	28.2	—	6.20	8.15	11.00	13.35	16.90	22.05
27	76.5	39.8	—	6.45	8.25	11.25	13.30	16.70	22.25
21	81.2	41.2	—	6.50	8.20	11.15	13.25	16.55	21.85
28	83.0	38.2	—	6.60	8.30	11.20	13.25	16.65	22.35
33	83.8	39.3	—	—	8.10	11.10	13.20	16.80	21.85
29	86.7	35.9	—	6.35	8.10	11.00	13.00	16.50	21.70
34	87.9	34.4	4.90	—	8.05	11.00	13.10	16.95	—
36	89.9	14.8	5.40	—	8.20	11.25	13.25	16.95	—
35	90.0	33.3	5.50	6.35	8.15	11.10	13.10	16.80	21.95
30	90.0	34.4	—	6.35	8.25	11.10	13.05	16.75	21.80
18	91.0	41.5	—	6.70	8.30	11.30	13.25	16.40	21.55
37	93.8	7.2	5.65	6.40	8.00	11.10	13.30	17.15	22.40
38	93.8	12.8	5.40	6.05	8.15	11.15	13.45	16.85	—
39	93.8	21.0	4.95	—	8.30	11.10	13.20	16.80	21.95
40	93.8	37.2	—	6.45	8.05	10.90	13.20	16.65	21.80
41	93.8	62.3	—	—	8.15	11.15	13.25	16.75	21.70
31	94.0	32.8	—	6.35	8.25	11.20	13.15	16.65	21.90
23	94.9	34.6	—	6.45	8.20	11.10	13.15	16.65	21.70
22	97.1	38.5	—	6.40	8.30	11.30	13.25	16.45	21.75
19	101.3	39.1	—	6.65	8.40	11.40	13.40	16.70	21.95
24	107.0	32.5	—	6.50	8.35	11.40	13.40	16.75	21.95
20	111.3	36.0	—	6.70	8.35	11.40	13.30	16.65	21.80
25	114.9	30.7	—	6.50	8.30	11.30	13.20	16.40	21.75
17	122.3	34.1	—	6.35	7.80	11.10	13.15	16.80	—
Mean			5.30	6.44	8.19	11.17	13.24	16.72	21.90

taken in succession, as will be seen from the numbers in the first column of Table I. Moreover, the humps in the curves at this voltage were always very small and the maximum usually difficult to locate. All this makes it appear unlikely that this feature could represent anything characteristic of the carbon monoxide molecule. Although this maximum could not be discovered in the blank runs, it does not appear impossible that it could be due to some type of inelastic collisions with the electrodes. There is a maximum at 4.6 volts in the curves for the electrons scattered from an incandescent silver target, which I obtained in an earlier investigation.* This is a good deal lower than the value here obtained; it is, of course, possible that the present maximum is a blend, but it is altogether too weak and diffuse to warrant any further discussion of the possibilities in this respect.

Carbon Dioxide.

This gas was prepared by heating sodium bicarbonate in a long evacuated glass tube,† connected by glass tubing to the evacuated storage flask as in the

* Rudberg, 'Proc. Roy. Soc.,' A, vol. 127, p. 111 (1930).

† Moser, "Die Reindarstellung von Gasen," p. 113, Stuttgart, 1920.

case of carbon monoxide. For the purpose of removing the water vapour formed, the gas was passed over calcium chloride, through a couple of wash bottles containing concentrated sulphuric acid and finally through a tube with phosphor-pentoxide.

Unlike carbon monoxide, the dioxide gave very much trouble when it was tried to run an oxide-coated cathode in the presence of the gas. Great difficulties were experienced in trying to keep the emission from the cathode steady. Sudden large changes in the current frequently occurred without any apparent cause. For not too high bombarding voltages, however, I found that this unsteadiness could mostly be avoided, if the content of barium oxide of the coating was reduced. Even when this was done and great care was taken not to overheat the foil, the active deposit would seldom last for more than two curves, after which the tube had to be opened up, a fresh coating applied and the cathode re-inserted and adjusted in a line with the slits. To avoid that conditions would alter too much in the course of a single series of measurements, both pressure and bombarding current were kept as low as possible. For the same reason, the voltage range covered is only from 74 to 106 volts.

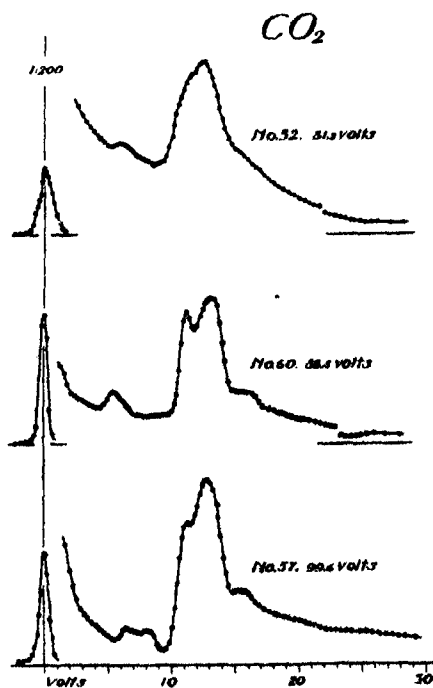


FIG. 2.

Owing to the experimental difficulties mentioned, the results for carbon dioxide are not as good as in the case of the other gases. The main features of the distribution curves, however, have been reproduced in most of the measurements. Thus the maximum close to 13 volts is the most conspicuous one in all the curves. Typical curves for carbon dioxide are shown in fig. 2. The energy values for the maxima in the measured curves have been collected in Table II, together with data for primary voltage, pressure and bombarding current in each particular case.

Table II.—Carbon Dioxide.

No.	Voltage.	$p.$ $\times 10^{-3}$.	Current. $\times 10^{-6}$.	V_1 .	V_2 .	V_3 .	V_4 .	V_5 .	V_6 .	V_7 .
70	74.7	17.6	35.6	—	—	7.35	8.15	10.95	12.70	—
69	78.7	17.7	35.6	5.60	—	7.35	8.40	11.45	12.60	16.30
71	81.2	16.7	35.6	5.00	6.30	7.55	8.50	11.45	12.95	15.70
52	81.2	16.0	35.6	—	6.10	—	—	11.05	12.45	15.80
68	83.1	18.5	35.6	5.85	—	—	—	11.40	12.80	16.25
53	83.3	15.3	35.6	4.00	—	7.00	—	11.30	12.65	15.80
72	84.9	17.3	35.6	—	—	—	—	11.60	13.45	16.00
67	85.2	19.2	35.6	—	—	7.00	—	10.75	12.45	15.70
59	86.8	17.2	7.83	5.15	6.40	—	8.30	10.90	12.35	15.35
54	87.4	15.1	35.6	5.00	—	7.00	—	11.30	12.90	16.55
51	87.4	16.0	35.6	—	6.20	—	—	10.40	12.55	15.65
61	87.9	23.2	7.83	—	—	7.35	—	11.55	13.45	16.00
60	88.5	16.9	7.83	5.55	—	—	—	11.20	13.20	15.70
73	89.0	24.0	35.6	5.05	6.50	7.20	8.65	11.05	12.80	15.35
62	90.0	21.7	7.83	5.45	6.70	—	—	11.10	12.85	15.80
74	92.3	23.4	35.6	4.70	6.40	—	8.70	11.15	12.90	15.85
55	95.2	22.2	35.6	5.80	6.85	—	—	11.25	12.95	15.55
66	95.3	19.8	35.6	5.20	6.60	—	8.25	11.00	12.95	16.10
63	96.1	20.6	7.83	—	6.35	—	8.40	11.00	13.05	15.70
56	97.3	21.4	35.6	—	6.55	—	—	11.45	13.05	16.10
57	99.6	21.0	35.6	—	6.40	—	8.25	11.20	12.80	15.80
64	101.8	20.0	7.83	—	6.55	—	8.60	10.95	13.15	15.75
65	105.7	19.6	7.83	5.70	—	—	8.05	11.45	13.45	16.00
58	105.7	20.7	35.6	—	6.65	—	8.70	11.35	13.30	16.10
Mean				5.24	6.47	7.23	8.41	11.22	12.91	15.87

It is obvious from these figures that the individual deviations from the mean value are larger than in the case of the two gases previously investigated. This is undoubtedly due to the considerable experimental difficulties in the case of carbon dioxide, which have been mentioned above. A considerable part of the latitude in the determination of the various maxima results from irregular changes in the zero of the voltage scale, i.e., from shifts in the position of the primary peak produced by the direct beam of electrons. Such shifts were mostly clearly indicated, when the zero was checked at the end of a run, and it was sometimes difficult to know how to correct for this change. It is

evident that changes in the contact potential of the electron source with respect to the slit system usually occurred, as the emitting cathode deposit was consumed in the discharge.

The 6.5 volts maximum appears strongly in the curves obtained in the blank experiments. There is also evidence of the maxima close to 5 and 7 volts in these curves, although the indication of the 7-volt maximum is somewhat faint. It is obvious that the strong 6.5-volt maximum is identical with the maximum found at the same position in the work on nitrogen and on carbon monoxide. The rather broad and not very well defined 5 volts maximum checks with the corresponding maximum from Table I; the surprisingly good agreement is largely accidental. From the present blank runs it is evident that the appearance of this maximum has nothing to do with electron collisions in the gas. It seems most probable that the same is true in the case of the faint 7 volts maximum, found in some of the measurements listed in Table II.

Discussion.

To facilitate the discussion of the results obtained the mean values from Tables I and II have been collected in Tables III and IV, together with the number of curves showing the maximum in question, the computed average error in each single determination, the probable origin of each maximum and the interpretation, discussed below, in such cases where a comparison with spectroscopical data or critical potential determinations has been possible. The position of each maximum is given both in volts and in wave-numbers, cm.^{-1} ; the reasons for representing the uncertainty in the tabulated mean values by the average error of a single determination, rather than by the computed error in the mean value, have been discussed in connection with the work on nitrogen.

Table III.—Carbon Monoxide.

	V_1	V_2	V_3	V_4	V_5	V_6	V_7
No. of determinations	6	20	25	25	25	25	20
Average error, volts.	± 0.31	± 0.16	± 0.13	± 0.14	± 0.13	± 0.18	± 0.22
Maximum, volts.	5.30	6.44	8.19	11.17	13.24	16.72	21.90
Maximum, cm.^{-1}	42,963	52,205	66,391	90,547	107,328	135,538	177,528
Origin	app.	app.	CO	CO	CO	CO	CO
Interpretation			A(0) 64,765 A(1) 66,247 A(2) 67,695 A(3) 69,108	B(0) 86,929 B(1) 89,011 C(0) 91,923 C(1) 94,056 E(0) 92,928	G 105,268	A'(0) 135,312 438 A'(1) 136,867 962 (2 V_5)	$V_6 + V_7$

Table IV.—Carbon Dioxide.

	V ₁ .	V ₂ .	V ₃ .	V ₄ .	V ₅ .	V ₆ .	V ₇ .
No. of determinations	13	14	8	12	24	24	23
Average error, volts.	±0.50	±0.20	±0.21	±0.22	±0.28	±0.32	±0.26
Maximum, volts.	5.24	6.47	7.23	8.41	11.22	12.91	15.87
Maximum, cm. ⁻¹	42,477	52,448	58,609	68,174	90,953	104,652	128,647
Origin	app.	app.	app (?)	CO ₂ (?)	CO ₂	CO ₂	CO ₂
Akesson (volts)	—	6.4	—	—	—	—	—
Löhner (volts)	—	6.3–6.8	—	—	11	13	—

I think that it is fairly obvious from the curves reproduced in figs. 1 and 2 and from the tables, that the results obtained for the two gases studied are distinctly different. Further, with the method adopted in which fresh gas is being pumped through the collision chamber continuously during the measurements, the chance for any possible new products formed to accumulate in the apparatus must be very small. It is therefore believed that the energy distributions for the scattered electrons which have been obtained are actually those characteristic of the gases introduced into the collision space.

In the case of CO critical potential measurements by Mohler and Foote,* using the method of Hertz, were interpreted by these investigators as showing characteristic energy losses of 6.0 and 8.0 volts. This would correspond to the excitation of the levels now usually denoted *a* and A, the initial states of the Cameron bands and the fourth positive carbon group, respectively. These and the other levels of carbon monoxide known at present are shown in fig. 3. The electronic levels for CO⁺ have been included at the top of the diagram, in such a way that the position of each level measures the energy of that particular state with respect to the normal state of the neutral molecule. Only such vibrational levels as are of interest for the present discussion have been drawn. The singlet system for the neutral molecule falls to the right in the figure, the triplet levels are shown to the left. A number of hitherto unclassified levels have been arbitrarily arranged between these two systems. The data for the positions of the levels are taken from the tables by Birge,† which have been confirmed by several later investigators.‡ The minimum potential differences

* 'Phys. Rev.', vol. 29, p. 141 (1927).

† 'Phys. Rev.', vol. 28, p. 1157 (1926); 'Int. Crit. Tables,' vol. 5, p. 409 (1929).

‡ Johnson and Asundi, 'Proc. Roy. Soc.,' A, vol. 123, p. 560 (1929); Asundi, *ibid.*, vol. 124, p. 277 (1929); Herzberg, 'Z. Physik,' vol. 52, p. 815 (1929); Eatsey, 'Phys. Rev.,' vol. 35, p. 309 (1930); Headrick and Fox, *ibid.*, vol. 35, p. 1033 (1930); Kaplan, *ibid.*, vol. 35, p. 1298 (1930).

required to excite the various spectra corresponding to transitions between these states have been experimentally determined by Duffendaack and Fox* and also by Hepburn.†

The positions of the maxima in the distribution curves of the present investigation have been marked off to the extreme right in fig. 3 from the data of

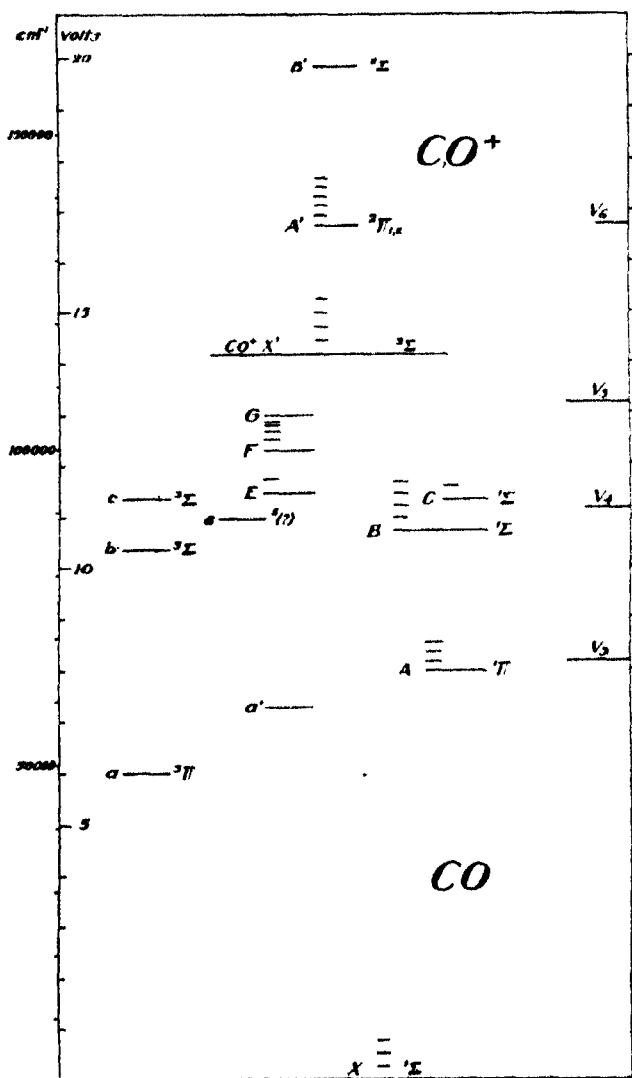


FIG. 3.

* 'Nature,' vol. 118, p. 12 (1926) and 'Astrophys. J.,' vol. 65, p. 214 (1927).

† 'Phys. Rev.,' vol. 29, p. 212 (1927).

Table III. Only values which are believed to be characteristic of the gas studied are shown. As indicated in Table III, the maximum V_7 is attributed to electrons which in their passage through the gas have suffered two inelastic collisions, one with a loss V_3 and the other with a loss V_6 . The position of the V_7 maximum is in reasonable agreement with this interpretation, considering the broad appearance of this hump in the curves. Double collisions should not occur very frequently at the pressures employed, and only the most common energy losses could contribute to this effect. The two maxima V_3 and V_6 are by a good deal the strongest ones observed. Furthermore, it appears that the relative magnitude of the V_7 maximum increases with pressure; the maximum is best developed in the curve for the highest pressure used, No. 41 (fig. 1). If this interpretation is correct, one would expect to find evidence in the distribution curves also of the double collisions $V_3 + V_3$ and $V_6 + V_6$. There is some indication, in part of the curves, of a very broad and low maximum in the region which should correspond to the latter process; this indication of a maximum appears to behave in the manner to be expected, when the pressure is increased (compare fig. 1). Two V_3 collisions would produce a maximum almost exactly in the same position as the maximum V_6 observed. It seems fairly certain that such a process contributes to the latter maximum, but there are several circumstances which make it unlikely that double collisions could be entirely responsible for this maximum, or even for a large part of it. The relative size does not change with pressure. A little consideration shows that the V_6 maximum must be much stronger than V_7 , although the proximity to the strong maximum V_6 tends to make the corresponding change in the curve small. It seems, therefore, that V_6 is due to some kind of single collision.

Returning to fig. 3, one would expect that the transitions resulting at the impacts of electrons with CO molecules would preferably take place from the normal X-state to the other singlet states A, B and C. It is true that some of the triplet series have been found in absorption and some of the corresponding levels excited at the calculated voltage. In the latter case, however, the efficiency appears to be small at low pressures. Thus Duffendack and Fox (*loc. cit.*) report that the intensity of the Cameron bands ($a \rightarrow X$) was too small to permit them to determine the excitation potential. Herzberg,* who used an electrodeless discharge for excitation, states that these bands are very weak. However, Mohler and Foote (*loc. cit.*) observed an energy loss corresponding to this level. The reason for these apparently somewhat contradictory results is not obvious; Mohler and Foote used pressures from 0.1

* 'Z. Physik,' vol. 52, p. 815 (1929).

to 0.7 mm. In the present work no maximum has been found corresponding to this level.

The strong maximum V_3 is attributed to the excitation of the first singlet state A. On the basis of the Franck-Condon* principle, the vibrational levels of this state which are most likely to be excited at an electron impact can be found, assuming that the initial level of the molecule hit is one of vibrational quantum number $v = 0$, since the temperature of the gas was scarcely very different from room temperature. In fig. 4 are drawn potential energy curves for some of the different electronic states of the neutral and the singly ionised carbon monoxide molecule, and the corresponding vibrational levels. The shape of these curves corresponds to the general function given by Morse,† and the constants used in calculating the curves are those computed by him from band spectroscopical data. The nuclear separation r_0 , corresponding to the lowest point of the energy curve, is known from a rotational analysis of bands; the value adopted for the normal X-state was recently given by Snow and Rideal‡ from infra-red investigations, and coincides with the r_0 value, which has been calculated by Morse using an empirical formula (*loc. cit.*). The vertical distances between curves for different states in fig. 4 are not to scale.

According to the new quantum mechanics the lowest vibrational level, of quantum number $v = 0$, falls above the lowest point of the potential curve by a definite amount. At the time when the Franck-Condon theory appeared it was assumed that this level was one of zero vibration, for which the nuclear separation was constant and equal to r_0 . According to this theory, therefore, for transitions involving one level for which $v = 0$, there should be only one maximum in the usual intensity distribution diagram for an electronic band system, but two maxima in the case of other vibrational levels. This is still true according to the new quantum mechanics, for although there is now a finite range of possible r -values in the state $v = 0$, the wave-function for this state has only one maximum corresponding to the distance r_0 , whereas there are at least two maxima of this function at the ends of the interval of possible r -values in the case of other vibrational levels. With the accuracy at present available, the difference between the old and the new picture (as regards the zero point energy) is unimportant in most practical cases.

* Franck, 'Trans. Faraday Soc.', vol. 21, p. 536 (1925); Condon, 'Phys. Rev.', vol. 28, p. 1182 (1926).

† 'Phys. Rev.', vol. 34, p. 57 (1929).

‡ 'Proc. Roy. Soc., A, vol. 125, p. 462 (1929).

The value of the experimentally determined energy loss V_2 is indicated by arrows in fig. 4. It will be seen that this maximum occurs just in the middle of

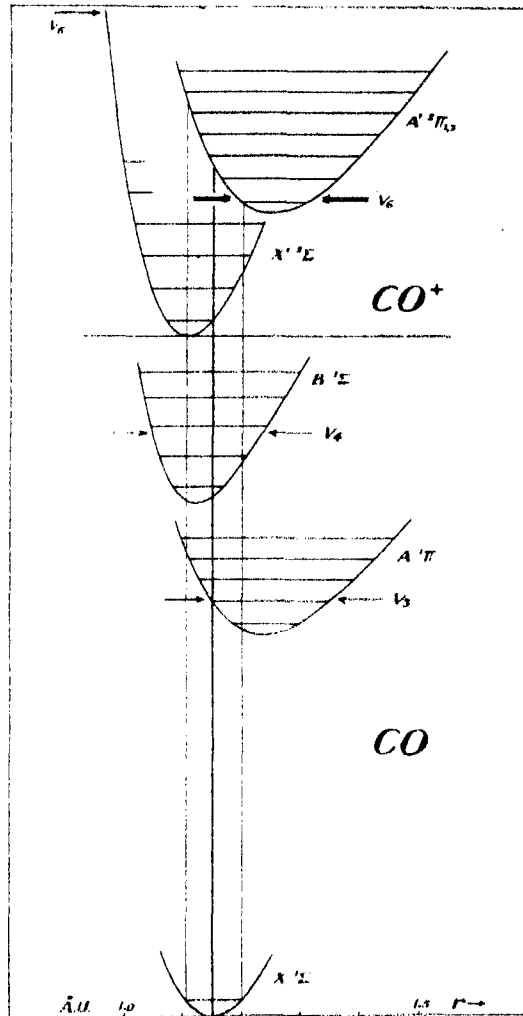


FIG. 4.

the group of vibrational levels for which the closest distance of approach of the two nuclei falls within the range of possible values for the nuclear separation in the lowest vibrational state of the normal molecule. This is in excellent agreement with the interpretation of this maximum here proposed and with the general ideas of Franck and Condon.

It is natural to attempt to correlate the V_4 maximum with the next singlet

state B in a similar manner. However, fig. 4 shows that this maximum falls decidedly above the vibrational levels to be expected in this case. Now from fig. 3 there is one further singlet state C fairly close to B. The potential curve for the former cannot be determined, since only one more vibrational level is known* for this state; from the rotational analysis by Johnson and Asundi†, $r_0 = 1.1220$. The high value of V_4 seems, however, to be satisfactorily accounted for, if this maximum is regarded as the unresolved result of excitations of both B and C. It is possible that a third state E contributes to the V_4 maximum, since transitions to this state have been found in absorption.* The second strong maximum, V_5 , appears to indicate the excitation of the first vibrational level or levels of the G state. If this interpretation is correct, the G state must show a rather high probability of excitation, at any rate under the conditions of these experiments. Unfortunately very little is known at present about this state. Only one single vibrational level has been measured; transitions to this level are stated by Birge‡ to occur in absorption. The lower F state has been found in emission to combine with the X state. From the potential curve for the former (not drawn in fig. 4) one would expect excitation of the $v = 0$, and possibly the $v = 1$ level belonging to this state. It is possible that such excitation contributes part of the rising curve to the left of the V_5 maximum. It would seem, however, that the probability for this excitation must be much smaller than that for the excitation process responsible for V_5 ; otherwise the F-excitation would certainly have given rise to a separate maximum in view of the magnitude of the difference between V_5 and F.

As in the case of nitrogen previously investigated, there is no discontinuity in the slope of the distribution curves at the first ionisation potential, 14.18 volts in the case of carbon monoxide. There is a very gradual slowing up of the steep drop to the right of V_5 , which sets in somewhere between 14 and 15 volts; this is probably due to ionisation. It is possible that V_6 indicates a maximum in the probability of such ionisation, when the ejected electron escapes with an energy equal to the difference between V_6 and X' . The magnitude of this difference may be estimated from the corresponding curve in fig. 3; V_c in the left top corner refers to this curve. There are, however, certain points which are in favour of a different interpretation. Transitions from state A' to X' in fig. 3 give rise to the so-called "comet-tail" bands. Duffendack and Fox (*loc. cit.*) were able to excite these bands at a voltage of

* Birge, 'Int. Crit. Tables,' vol. 5, p. 409 (1929).

† 'Proc. Roy. Soc.,' A, vol. 123, p. 560 (1929).

‡ Birge, 'Int. Crit. Tables,' vol. 5, p. 409 (1929).

16.9 volts, and Hepburn (*loc. cit.*) obtained the first bands at 16.7 volts. This proves that the A' state is excited from the normal state of the neutral molecule by single electron impact. Furthermore, Duffendack and Fox state that the comet-tail bands form a typical low-pressure system, which outrivals other strong bands such as the B $\rightarrow$ A system at pressures of the order 0.05 mm., and that the comet-tail bands become very brilliant at higher voltages. In view of this one could attempt to attribute V_6 to direct excitation of the A' state from the normal X state of the molecule. The potential curve at the top of fig. 4 corresponds to the A' state. Since this is actually a doublet state, there ought to be two potential curves, running parallel, and two levels for each vibrational quantum number. To simplify the drawing of the diagram I have instead chosen to indicate the V_6 maximum by double arrows, which for the present purpose obviously amounts to the same. Fig. 4 shows that in any case the V_6 maximum falls well within the limits to be expected on the Franck-Condon theory.

Very few critical potential determinations have been published for carbon dioxide. Mayer* gives the ionisation potential as 12.5 volts. Åkesson,† using retarding electric fields for velocity analysis, found energy losses of 6.4 volts for slow electrons. Hughes and Dixon,‡ who employed the method of Franck and Hertz, give 10.0 volts for the ionisation potential.§ Later Mackay|| has obtained a value of 14.3 volts for the energy required to produce ionisation in CO₂.¶ None of these seem to bear any relation to the maxima obtained in the present work, unless the effect at 6.4 volts is masked by the maximum due to the slits; from analogy with the similar measurements on nitrogen and on carbon monoxide one would scarcely expect a maximum in the distribution curves at the ionisation potential. Quite recently the energy loss at 6.4 volts has been confirmed and two further losses of about 11 and 13 volts found,** probably corresponding to V_5 and V_6 . Spectroscopic work on carbon dioxide has not progressed far enough to make it possible to draw a level diagram of the different electronic states of the CO₂ molecule. Some

* 'Ann. Physik,' vol. 45, p. 1 (1914).

† 'Lunds Univ. Årsskrift,' vol. 12, No. 11 (1916).

‡ 'Phys. Rev.,' vol. 10, p. 495 (1917).

§ Interpreted by Franck and Jordan, "Anregung von Quantensprüngen durch Stösse," p. 286, Berlin, 1926, as an excitation potential.

|| 'Phys. Rev.,' vol. 23, p. 553 (1924).

¶ The most recent determination of this potential by Smyth and Stueckelberg, 'Phys. Rev.,' vol. 36, p. 472 (1930), gives 14.4 volts.

** Löhner, 'Ann. Physik,' vol. 6, p. 50 (1930).

absorption bands have been recorded by Leifson* in the far ultra-violet, but they do not seem to correspond to any of the maxima listed in Table IV.

Absence of Evidence for the Ionisation of Soft X-Ray Levels.

A few measurements for higher bombarding voltages have been obtained, in which the deflecting electric field was varied so as to give the entire distribution curve for all velocities of the electrons from zero to the value for the primary beam, in the manner described in the paper on nitrogen. Bombarding voltages up to 863 volts were used with carbon monoxide, and up to 750 volts in the case of carbon dioxide. The regions of the curves in which energy losses due to ionisation of the K-levels of oxygen and carbon would be expected were covered by a large number of closely spaced points. Since the curves obtained are of the same shape as the one reproduced in the paper on nitrogen, I have not considered it necessary to add another figure to those of the present paper. No evidence of the ionisation processes in question has been found. In the case of carbon monoxide the upper limit for the relative probability of such processes from the measured curves is about the same as in the case of nitrogen. With carbon dioxide it was extremely difficult to avoid sudden arcing in the tube, when a curve was taken at these high voltages, and it was necessary to use a rather small bombarding current. Hence the test for the absence of high energy losses is not as rigorous in this case as for the two other gases. In any case the present results confirm the conclusion that ionisations of the deeper electronic levels are very unfrequent for electron velocities of the magnitude here used.

Summary.

Previous measurements of the characteristic energy losses suffered by electrons in nitrogen at low pressures have been extended to the two gases carbon monoxide and carbon dioxide. The energy distribution of the electrons after passing through the gas shows several well-marked maxima which have been measured for different voltages and pressures. These maxima are characteristic of the energy levels of the particular kind of molecules under investigation. In the case of CO the various maxima found have been correlated with transitions from the normal state of the molecule to excited states known from the analysis of the band spectra belonging to this molecule or to singly ionised carbon monoxide. In those cases where a maximum has been attributed to a single electronic level, a study of the potential curves for the molecule shows the position of the maximum with respect to the different possible vibrational levels to be in accordance with the Franck-Condon theory.

* 'Astrophys. J.,' vol. 63, p. 73 (1926).

The Sorption of Carbon Tetrachloride at Low Pressures by Activated Charcoals. Part IV.

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(Received October 7, 1930.)

Introductory.

In this paper, the following points are dealt with :—

(1) In Part II of this series,* the effect of a variation in the evacuation temperature on the nature of the subsequently determined isothermal was investigated in the cases of charcoal C and D. The results indicated that, if displacement of oxygen from the surface of the charcoal were complete, the evacuation temperature (up to 800° C.) was unlikely to have much effect on the isothermal. In Part III† it was suggested that the isothermals might perhaps prove to be identical, allowance being made for any minor differences in surface structure brought about during the elimination of the oxygen. Further experiments have been done which, whilst indicating that the effect of high temperature degassing can be much greater than was found in Part II, support the views already put forward on the part played by adsorbed oxygen (experiments 1 to 5).

(2) In Part III the point was raised whether or not any of the determined isothermals were definitive, in the sense that no further drift in the direction of higher q/p ratios would take place on repeated further sorptions and desorptions. It was doubted whether this was so. If it were, it seemed that it might be the case when using the chemically activated charcoal B. Further work with B has however shown that isothermals with appreciably higher q/p ratios than were found in Part II can be obtained (experiment 6).

(3) It seemed desirable to have an independent test of the validity of the Pirani gauge pressure readings. Consequently an isothermal has been determined over a large pressure range (3.3×10^{-2} to 70.45 mm.) in a single experiment, the higher pressures being read by a mercury manometer, and the lower by the Pirani gauge. The results show that the readings of the latter instrument are valid (experiment 7).

(4) "Breaks" had been found in the different isothermals and isosteres at a pressure of about 0.1 mm. (Part II), and in Part III it was mentioned that the

* 'Proc. Roy. Soc.,' A, vol. 129, p. 235 (1930).

† *Ibid.*, p. 252.

existence of these breaks seemed to be a case of a more general phenomenon. In particular, Mr. L. J. Burrage, working in this laboratory and using a different method,* has found that, in presence of air, the isothermal of carbon tetrachloride on charcoal B is composed of a series of loops, covering the whole pressure range studied from 30 mm. down to 0.1 mm. at 25°. A section of the carbon tetrachloride isothermal of this charcoal, air being absent, has therefore been examined in detail, the pressures being measured by the mercury manometer. Ample evidence of discontinuities and breaks was found (experiments 7 and 8).

Experimental.

In all the Pirani gauge measurements recorded in this paper, the fully developed technique as described in Part I† of this series was used.

Experiment 1.—A specimen of charcoal A, degassed at 110°, was charged to 30.2 mg. per gram and its pressure measured; a second sorption point was followed by two desorption points, two sorption points and then by six alternate desorption and sorption points, finishing with point 12 at 70.3 mg. per gram. The maximum q value was 80.0 mg. per gram (point 10). The results are shown in fig. 1 (crosses). In order not to complicate the diagram, points 6 to 8 are not joined up, the first and last loops only of the isothermal being drawn. The line AB represents the best isothermal drawn through the points obtained in Part II, experiment 3, in which an initial charge of 135 mg. per gram had been put on the charcoal. Although in the present experiment the initial charge was low, and the initial q/p ratio consequently also low, the isothermal obtained is seen soon to cross AB, and the last point shows a very definite drift to higher q/p values. The *apparent* nature of the reversibility found in Part II, experiment 3, is thus made clear; it was indeed indicated by the position relative to AB of the derived isothermal obtained for this charcoal (see Part II, fig. 2).

Experiment 2.—A specimen of A was thoroughly degassed at 800°, and charged to 33 mg. per gram, at which the first pressure reading was made. There followed four more sorption points (5 = 112.5 mg. per gram), three desorption points (8 = 64.6 mg. per gram) and finally three sorption points (11 = 109.7 mg. per gram). As the isothermal was showing drift, the charcoal was allowed to stand overnight at 25°, and the CCl_4 pressure measured the next day. It had fallen from 1.81×10^{-2} to 1.73×10^{-2} mm., in agreement

* 'J. Phys. Chem.,' vol. 34, p. 2202 (1930).

† Chaplin, 'Proc. Roy. Soc.,' A, vol. 121, p. 344 (1928).

with the observed drift. The results are plotted in fig. 1 (black circles). It will be seen that the effect of the higher degassing temperature has been to

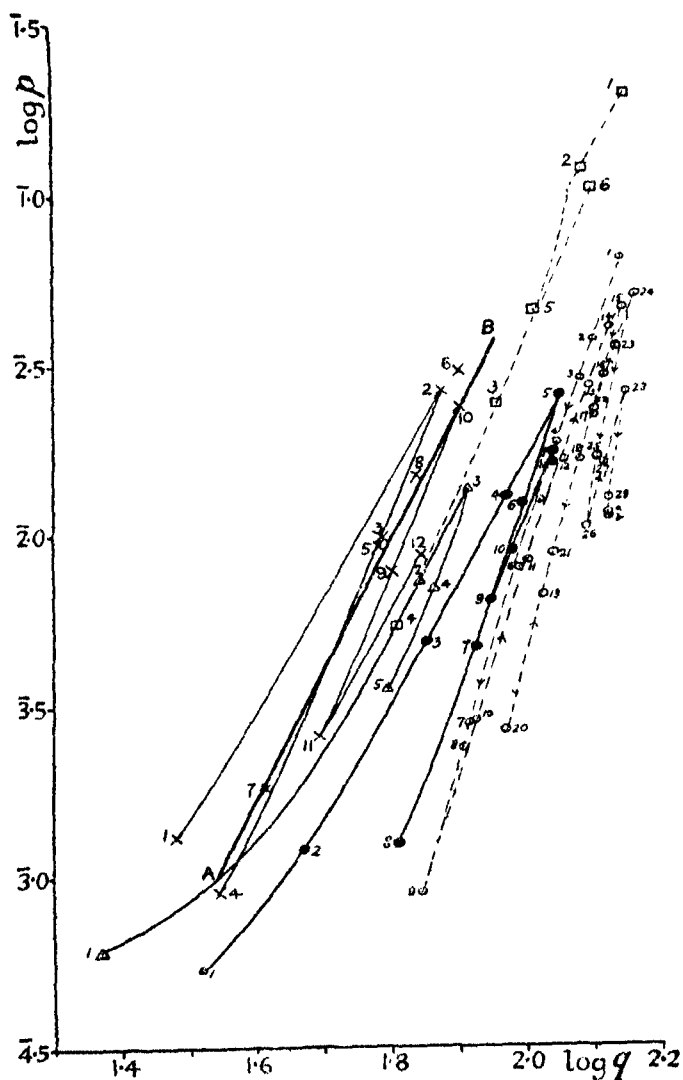


FIG. 1.

increase the initial q/p ratios at low charges above those found in experiment 1, thus confirming the results found in Part II with charcoals C and D. The difference between the isothermals of the "110° C." and "800° C." charcoals is, however, far greater in the present case. Whereas, for example, at 10^{-2} mm.,

the first desorption branches in the case of charcoal D were practically independent of the evacuation temperature and, in the case of charcoal C, the q values only differed by about 6 per cent., the increase in capacity of the "800° C." over the "100° C." charcoal A is found to be nearly 60 per cent.

Experiment 3.—An attempt was made to eliminate the drift found in the last experiment by charging the charcoal to a high initial pressure. A sample of A, degassed as before at 800°, was charged up to about 140 mg. per gram, the displaced gases removed at 90° as thoroughly as possible, and the first point taken at 138.5 mg. per gram and 6.78×10^{-2} mm. Eight more desorption points ($9 = 70.1$ mg. per gram and 9×10^{-4} mm.) were followed successively by six sorption and five desorption points, four sorption and two desorption points, two sorption and a final desorption point ($29 = 133.1$ mg. per gram and 1.33×10^{-2} mm.). At the end of the run, the charcoal was allowed to stand, as in experiment 2, and its pressure observed. One day later, during which the container had been heated to 80° C. for 1 hour, the pressure had fallen to 1.20×10^{-2} mm. (point 29a); after another day, during which the temperature had been kept throughout at 25°, the pressure was 1.17×10^{-2} mm. (point 29b).

The results are plotted in fig. 1 (circles). The drift with this charcoal, in spite of the original high charge, is seen to be remarkable, and indeed was as pronounced at the end as at the commencement of the run, a fact which clearly did not support the suggestion (see Introduction) that the definitive isothermals for "110°" and "800°" charcoals would be practically coincident.

During the evacuation of charcoals at 800° C., it has been noticed that an appreciable amount of a sublimate condenses in the colder parts of the tube. In the case of charcoal A this amounts to 0.6 to 0.7 per cent. of the weight of the original dried charcoal, and consists essentially of the chlorides and sulphates of sodium and potassium.* This fact suggested that the increase in sorptive capacity resulting from 800° C. evacuation might be caused by the elimination of the sublimate having made available parts of the charcoal previously occupied by inorganic constituents, the drift arising from the relative "inaccessibility" of the charcoal surface or cavities thus set free. If such an increase in accessible surface were actually to take place, whether due to the removal in this manner of inorganic constituents or to the slow burning away of carbonaceous "obstructions," it seemed probable that the charcoal, once treated in this way, should retain the relatively high sorptive capacity of an "800° C." charcoal after admission of air at ordinary temperatures, with subsequent

* Hand and Shiels, 'J. Phys. Chem.,' vol. 32, p. 453 (1928).

degassing at 110° . If, on the other hand, the effect of the high temperature degassing and the cause of the drift were dependent on the elimination of combined oxygen from the charcoal surface, an isothermal determined on a charcoal which had been (i) degassed at 800° , (ii) exposed to air at room temperature, (iii) degassed at 100° , should resemble that for a " 110° C." charcoal. This point of view was tested.

Experiment 4.—A specimen of charcoal A was thoroughly degassed at 800° C. It was then cooled down, exposed to air for 18 hours, re-evacuated at 110° C., and a five-point isothermal determined, commencing with the low q figure of 23.4 mg. per gram. The results are shown in fig. 1 (triangles). It will be seen that the points lie at higher p/q ratios than those of experiment 2 (" 800° C." charcoal) and that the drift on desorption is normal.

Experiment 5.—A similar experiment to No. 4 was carried out, but, in this case, the charcoal was exposed to air for 6 months before evacuation at 110° , and a high charge of CCl_4 (141.8 mg. per gram) was used for the first point of the isothermal. The total number of measured points was six, and the results are plotted in fig. 1 (squares). When these are compared with the points of experiment 3 (the pressure at 138.5 mg. per gram is nearly three times the pressure at point 1 of experiment 3, where the q value is the same) and with the line AB (on an extension of which, assuming a "break" at 0.1 mm., the first two points of the present isothermal practically fall), there is little doubt that the charcoal in the present case has behaved as an " 110° C.," and not as an " 800° C.," charcoal.

We therefore regard the results of the last two experiments as supporting our views on the essential nature of the effect of high, as compared with low, temperature evacuation.

Experiment 6.—A specimen of charcoal B was evacuated at 110° , charged up to about 90 mg. per gram, and the first point taken ($q = 88.7$ mg. per gram). Six desorption points were then measured ($7 = 14.0$ mg. per gram and 2.9×10^{-4} mm.), followed by 12 sorption points ($19 = 213.3$ mg. per gram and 0.270 mm., very near the limit of measurement of the Pirani gauge). The results are plotted in fig. 2 as triangles, in the form both of $\log p/\log q$ and also p/q diagrams (the points at the three lowest pressures are not included in the latter case). ABC represents the derived isothermal obtained for this charcoal in Part II (fig. 3), and it is seen that the points of the present experiment all lie at higher q/p ratios than formerly. The doubt previously expressed as to whether any of the isothermals obtained in Part II were characteristic of the charcoal concerned is therefore justified. And this fact is made even

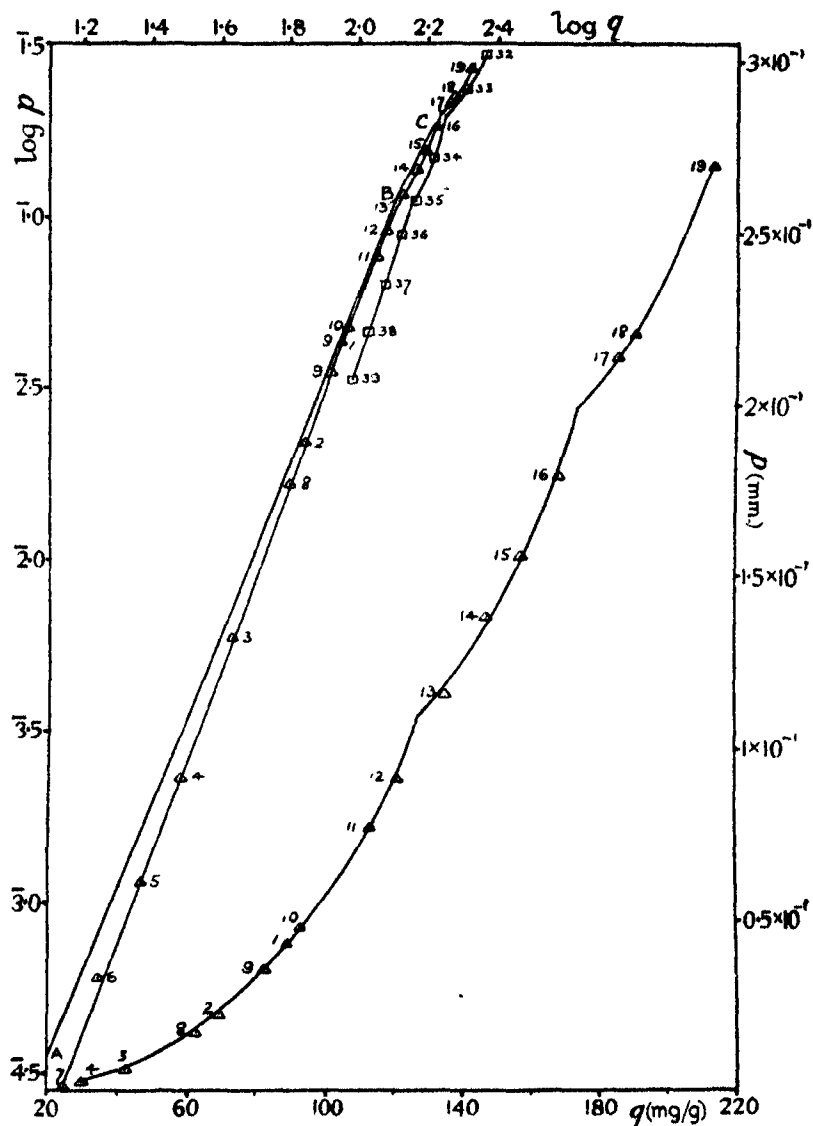


FIG. 2.

clearer by points 33 to 39 (denoted by squares), taken from the next experiment, in which a very much higher charge of sorbate had been put on the charcoal in the course of the run.

An examination of the $\log p / \log q$ plot shows that, starting from low pressures, the isothermal is practically linear up to point 10, and then deviates slightly in the direction of lower pressures. Above point 12, this deviation

becomes more marked, and there is definite evidence of "breaks." One way of drawing the isothermal would be to put in such breaks between points 10-11, 12-13 and 16-17 respectively. The first of these, however, means a break in the region of 0.06-0.07 mm. As no break at such low pressures has been found in other cases in CCl_4 isothermals, using either the vacuum technique or the retentivity technique developed in this laboratory,* we prefer to draw the isothermal as shown, *i.e.*, as being continuous up to just above 0.1 mm., with breaks at this point and at about 0.2 mm., and, when logarithmically plotted, very slightly convex to the $\log p$ axis just below the first break.† The low pressure portion of the isothermal of experiment 7 (squares) has been drawn in such a way as to agree with this interpretation of the data. We realise that such a procedure is somewhat arbitrary, and that very little more can be concluded with certainty from a single isothermal of which the points are spaced as in the present case beyond the qualitative fact that "breaks" do occur. To find the position of these breaks, more experimental points are required on the isothermal. In the present case, breaks have been found by the retentivity method in the CCl_4 isothermals for a large number of charcoals (including B), centring on pressures of about 0.105, 0.145, 0.185 and 0.26 mm.

Experiment 7.—The charcoal specimen used in experiment 6 was allowed to stand at room temperature for 2 weeks after the determination of the last point, at which the measured Pirani gauge pressure had been 0.27 mm. Its equilibrium pressure, when then measured by a U mercury-manometer attached to the apparatus,‡ was found to be about 0.21 mm. Three possibilities could account, wholly or partly, for this difference in pressure, *viz.*, (a) inaccuracy in the mercury manometer reading, (b) an error in the Pirani gauge reading, which was being used very near to its possible limits of measurement, and (c) a fall in pressure on standing, due to drift or slight displacement of gas.

The third possibility was unfortunately not tested at the time. With regard to the first, the error of the mercury manometer, which was giving trouble at this stage, was estimated as at least 0.05 mm., although, in the present case, readings after three successive re-adjustments of the mercury meniscus gave 0.20, 0.22 and 0.22 mm. In order to test thoroughly the second possibility, it was decided to carry through a determination of the CCl_4 isothermal on this

* Burrage, *loc. cit.*

† It was suggested in Part III that this type of q/p relation might be found in isothermals on thoroughly clean charcoals.

‡ Part I, pp. 349-350.

charcoal up to high pressures, determining first a series of sorption and then of desorption points, and, finally, when the pressure on the desorption branch had fallen sufficiently low, changing over from the mercury manometer to the Pirani gauge. Any abrupt discontinuity at this point would be evidence of some kind of error in the readings of the Pirani gauge.

A further specimen of charcoal B was evacuated at 110°C ., charged to about 200 mg. per gram, and the first point measured at 199.6 mg. per gram and 0.28 mm. Fifteen further sorption points were taken, the majority at intervals of about 80 mg. per gram (point 16 = 1313.5 mg. per gram and 70.45 mm. pressure). Desorption was then commenced. Fifteen points were measured using the mercury manometer (31 = 239.3 mg. per gram and 0.32 mm.). The earliest of these points were relatively close together, the spacing becoming wider later. With point 32 (234.1 mg. per gram and 0.296 mm.) readings with the Pirani gauge were commenced and continued to the last point measured (No. 39 = 95.5 mg. per gram and 0.03325 mm.). Except when obtaining the first sorption and the last three desorption points, the charcoal was not heated above 25°C . during the whole experiment.

The results are plotted logarithmically in fig. 3, where sorption points are represented by triangles and desorption points by squares and circles, according to whether the pressure measurements were made with the mercury manometer or with the Pirani gauge respectively. The single black circle is the last point of experiment 6 as determined by the Pirani gauge, and the single cross the same point as measured later by the mercury manometer. A section of the results is shown inset, plotted on an expanded scale.

The two portions of the desorption curve depending on the mercury manometer and on the Pirani gauge respectively are seen to join on to one another satisfactorily. Moreover, the Pirani gauge reading of point 19 of the preceding experiment practically falls on the same curve (see also fig. 2), whereas the mercury manometer reading lies well below it. We conclude therefore that the Pirani gauge measurements in general are valid, and that the discrepancy noted above between the two pressure readings of the point in question was most probably due to the unsatisfactory behaviour at the time of the mercury manometer.

The next point to note is that, whilst at intermediate pressures there is very little tendency for the desorption points as a whole to lie at higher q/p ratios than the sorption points, this is not the case at the highest pressures (see inset). This fact, which can hardly be accounted for by experimental error in pressure reading, requires explanation. One would imagine that, if any displacement of

gas had taken place at the maximum charging pressure, with consequent drift towards lower pressures, this drift would be manifested at lower q values by

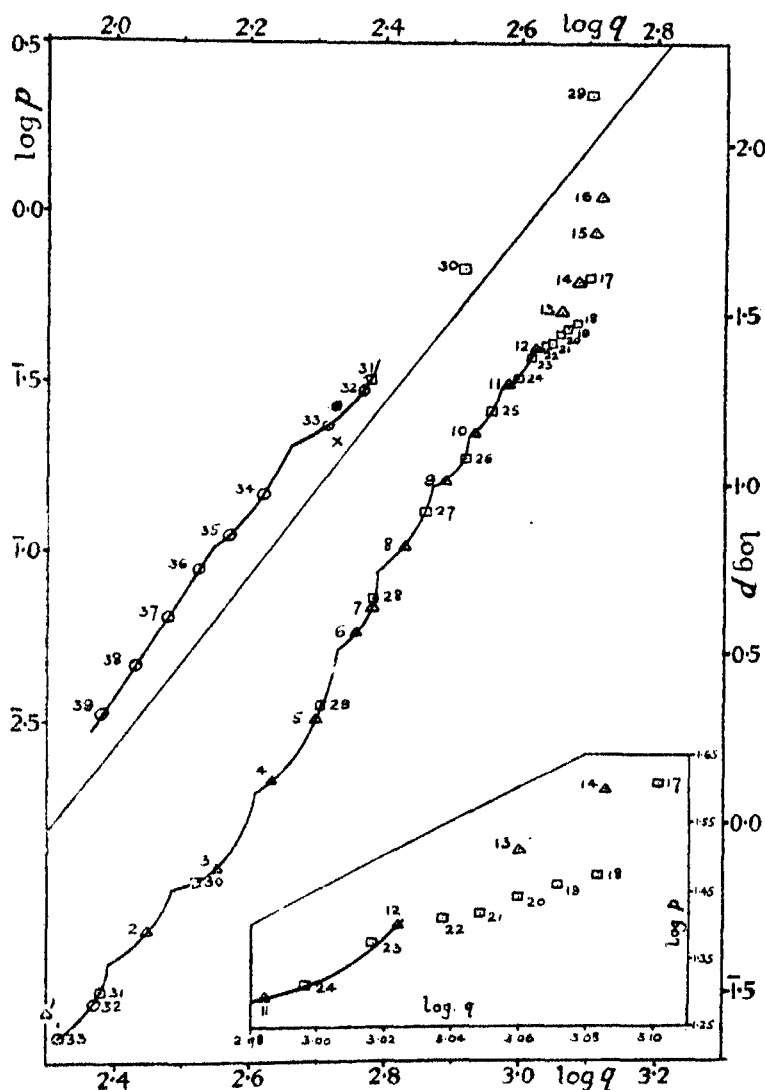


FIG. 3.

an ever increasing distance between the sorption and desorption branches of the isothermal (e.g., as in fig. 1). We think that the explanation may lie in the fact that the tap-grease on the container was becoming heavily charged

with CCl_4 during sorption at these high pressures,* and that there was an initial delay in the evolution of this dissolved CCl_4 as the pressure was lowered during desorption. If this view be accepted, it would indicate (i) that the q values at the highest pressure are too great, particularly, of course, those on the desorption branch of the isothermal, and (ii) that, at a pressure of 0.6 to 1 mm. during the sorption process, *essential* gas displacement had been completed, as evidenced by the practical coincidence of the sorption and desorption branches of the isothermal over a considerable pressure range above this point. By *essential* gas displacement, we mean the displacement of that gas which is of significance for the pressure of the sorbed CCl_4 . That carbon dioxide was still being given off from the charcoal was demonstrated during the measurement of points 32-39 with the Pirani gauge, the average pressure of this gas in the CCl_4 vapour phase being 5×10^{-4} mm.

Lastly, it must be noted that it is quite impossible to draw a single smooth curve through either the sorption or the desorption branch of the isothermal, the experimental points being removed from any such smooth curve by amounts considerably in excess of the experimental error. This again is evidence of the discontinuous nature of these isothermals. As in experiment 6, however, whilst the data suffice to exhibit the fact of discontinuity, they do not suffice to determine the positions of the breaks. The points below No. 12 have been joined up in order better to emphasise the discontinuous structure, but no stress whatever is laid on the detail of the curve, as it is clearly possible to draw the isothermal in other, quite different, ways, alike only in exhibiting breaks.

Experiment 8.—As, at this stage, measurements by Mr. L. J. Burrage on the isothermal of CCl_4 on charcoal B at 25° , carried out by the retentivity method, were available, and as these measurements pointed to the existence of a large number of well-defined breaks, it was decided to study a section of the same isothermal intensively by the technique employed in experiment 7, taking points at close intervals, with the intention of seeing whether the breaks, of which the existence was indicated in experiment 7, could be more closely defined, and, if so, whether the p/q values at which they appeared were coincident with those found by Mr. Burrage. The pressure region chosen for examination

* The total weight of evacuated charcoal in this experiment was 1.9774 grams, and of tap grease 0.0242 gram. The maximum difference between the sorption and desorption curves in the high pressure region was about 80 mg. per gram or 0.16 gram. At the maximum charging pressure, the tap grease was actually observed to show signs of "running."

was 18 to 31 mm. The breaks found by the retentivity technique in this range lay at 17.7, 19.1 (18.8), 21.0 (21.0), 22.2 (22.2), 23.4 (23.3), 25.0 (24.9), 25.8 (26.1), 27.6 (27.6) and 30.5 (30.2) mm. The bracketed figures represent the average pressure values at which breaks were found for some half-dozen different charcoals.

A specimen of B, degassed at 110°, was charged up in the usual way to about 1150 mg. per gram, and the first point measured at 1142.2 mg. per gram and 31.74 mm. Twenty-one further desorption points were then determined. In order that they should be closely adjacent to one another, a procedure was adopted very similar to that described at the commencement of Part III. After attaching the freshly-weighed charcoal container to the apparatus the latter was evacuated and then filled with CCl_4 vapour to a measured pressure only slightly less than the equilibrium pressure of the preceding point, before opening up the container to the apparatus. The consequence was that the loss of sorbate from the former to the latter was small, and the system readjusted itself to new p and q values only slightly lower than those which characterised the preceding point. Throughout the whole experiment, including the initial sorption, the temperature of the charcoal did not exceed 25° C. The results are shown in fig. 4, in the upper curve as $\log p$ against $\log q$ (triangles) and in the lower as p against q (squares). The full black triangles and squares (Roman numerals) represent such points of experiment 7 as fall within the range of the present experiment. When it is remembered that the scale on which the upper curve of fig. 4 is plotted is about ten times that of fig. 3, and that reason has been given for supposing points XX and XXI (20 and 21 of experiment 7) to lie at too high q values, the agreement between the two sets of measurements must be regarded as satisfactory.

In drawing the isothermals, we set out from point 1, and the curves as shown appear to us to give the most probable interpretation of the data. With regard to the exact definition of the position of the breaks, the present experiment is more satisfactory than experiment 7, but not completely so; the gaps between the different points, averaging 10 mg. per gram, are still too great. As drawn, the isothermal shows breaks (mean values from the two plots) at 28.45, 25.7, 24.8, 23.85, 23.05, 21.5, 20.55, 19.4 and 18.35 mm. Except for the second and third of these, the agreement with the values of the breaks found by the retentivity technique (see above) is poor. By drawing the isothermal in such a way as to place a break between points 14-15 instead of between 15-16 (such a possibility would be as likely as the one actually adopted) a break would be

obtained at about 22.2 mm., in agreement with the retentivity results. Alternatively, it would be possible to omit a break in this region altogether,

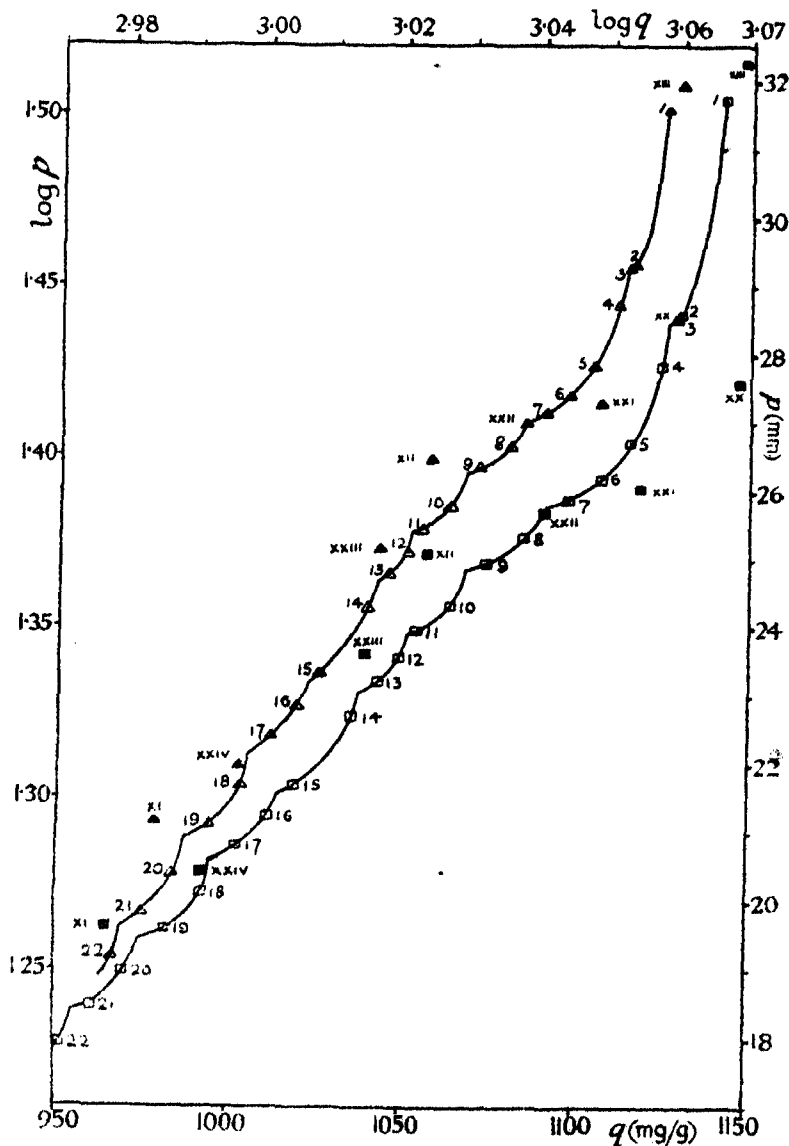


FIG. 4.

and to draw a single curve through points 14-17. But that the data are insufficiently numerous is best seen by drawing the isothermal commencing with point 22 and not with point 1. The result is again a broken curve, but

with its discontinuities at pressures different from those found in the curve as drawn.

Whilst the present experiment affords further evidence of the discontinuous nature of these isothermals (the mercury manometer was working satisfactorily, and the error in the final pressure values, each the mean of a number of separate readings, is estimated as 0.02–0.03 mm. only), it can not be said to have made any definite contribution to the quantitative side of their study. For this purpose a less laborious method of experimentation is necessary. Some such measurements have been done, and others are in progress.

Summary.

1. Experiments are described which support the view that the effect of high temperature pre-evacuation of a charcoal in increasing its initial sorptive power for a vapour is due to the more efficient removal of adsorbed oxygen, and not to an increase in total surface available for adsorption.

2. Evidence is brought to show that whilst, in the case of a chemically-activated charcoal and carbon tetrachloride, a charging pressure of about 0.1 mm. at 25° is insufficient to clean up adsorbed oxygen from the charcoal surface, this can be effected in practice by a charging pressure of 1 mm.

3. The Pirani gauge has been shown to give pressure readings which concord with those of a mercury manometer.

4. Evidence is brought in support of the view that the isothermals of carbon tetrachloride on charcoal are discontinuous in structure. The technique employed proved inadequate for the purpose of the quantitative definition of these discontinuities.

The experiments described in this paper were carried out between August, 1926, and July, 1927.

*The Sorption of Water Vapour at Low Pressures by
Activated Charcoals.—Part I.*

By A. J. ALLMAND, F.R.S., and R. B. KING, King's College, London.

(Received October 7, 1930.)

Previous work* has led to the accumulation of many data on the sorption of water vapour by activated charcoals. Comparatively few measurements at pressures less than 1 mm. have, however, been carried out, and the purpose of the present experiments, of which the first results are described below, is to fill this gap. The nature of charcoal—water vapour isothermals at low pressures is indeed of considerable interest, as in their form at higher pressures they differ widely from the isothermals given by the great majority of gases and vapours.

Experimental Method.

This was very similar to that worked out by Chaplin† in connection with low pressure carbon tetrachloride isothermals. The water supply was contained in a small bulb sealed on to the apparatus. It was freed as far as possible from dissolved carbon dioxide and permanent gases by the continued application of the cycle (i) freezing at the temperature of solid carbon dioxide and ether; (ii) evacuation; (iii) melting—until the residual pressure over the ice at -78°C . was practically unchanged by further treatment. Owing to the solubility of carbon dioxide in ice, this gas could not be completely removed and, in the actual experiments, a charging pressure of water vapour of about 10^{-1} mm. contained about 10^{-4} mm. pressure of carbon dioxide.‡

The charcoal in every case was degassed beforehand at 110°C . until the pressure (at that temperature) had fallen to $0.75\text{--}1.5 \times 10^{-4}$ mm. (measured on the McLeod gauge). After attaching the evacuated and weighed container to the vacuum apparatus, the latter was evacuated until the Pirani gauge registered within 0.05 volt of the zero figure. The container was then opened up to the apparatus, and the last traces of gases and vapours removed by connecting with the clean-up charcoal at liquid oxygen temperature.

* 'J. Phys. Chem.,' vol. 33, pp. 1151, 1161, 1682, 1693 (1929).

† 'Proc. Roy. Soc.,' A, vol. 121, p. 344 (1928).

‡ In subsequent experiments, an alkaline solution will be used in the supply bulb.

As previous experience* had indicated, mere evacuation at 110° was insufficient to expel all gases, including carbon dioxide, from the charcoal; displacement of these by the sorbate was necessary. For this purpose, the charcoal was exposed to a charging pressure of water vapour of about 10^{-1} mm., this being regulated by raising and lowering a vacuum flask containing solid carbon dioxide and ether under the water supply bulb. After charging in this way, the container tap was closed, and the charcoal raised to a temperature of 90° by means of a vacuum flask containing hot water, adjusted to such a height as to make the upper levels of the charcoal and the water coincide. The container was then opened to the apparatus, and the pressure of the gas phase investigated by the Pirani gauge (i) with the freezer at room temperature, giving a rough measure of the total pressure (water vapour, carbon dioxide, permanent gas); (ii) with the freezer at -78° (carbon dioxide and permanent gas only); (iii) with the freezer at liquid oxygen temperature (permanent gas only). The whole of the gas phase was then removed by means of the clean-up charcoal.

To determine a sorption point, the charcoal, now "free" from carbon dioxide and other gases, was charged at about 10^{-1} mm. pressure of water vapour until the pressure over it had reached the required value. The container was shut off, the apparatus cleaned up overnight, the container then opened up to the apparatus, and the pressure, when constant, read on the Pirani gauge. The gases were then analysed for carbon dioxide in the usual way. Appreciable amounts were generally found at this stage, in which case the charcoal was again shut off, and the vapour phase removed on the clean-up charcoal. On subsequently re-opening the charcoal to the apparatus and measuring the pressure, amounts exceeding a pressure of about 10^{-4} mm. of substances other than water vapour were only found in exceptional cases. The amount of water vapour taken up at the measured pressure was determined by direct weighing.

To determine a desorption point, the test charcoal was opened up to the clean-up charcoal (at liquid oxygen temperature) until the required pressure had been reached. For pressures lower than 10^{-2} mm., an additional freezer at liquid oxygen temperature was used to accelerate matters and, for the lowest pressures, hot water was placed around the test-charcoal container. The subsequent measurement of the pressure, analysis of the vapour phase for displaced carbon dioxide, and measurement of the water sorbed were carried out as above.

* 'Proc. Roy. Soc.,' A, vol. 129, p. 235 (1930).

The Pirani gauge α value for water vapour was taken as 0.0237.* The charcoals used have all been described elsewhere. They are denoted, as before, by the letters, A,† B,‡ C,§ H,‡ K,§ L,§ All measurements, unless otherwise mentioned, were made at 25°.

Results.

One set of experimental figures is given in full, as a specimen of the type of result obtained. The results as a whole are shown in figs. 1 and 2.

Charcoal A.—The data obtained are given in Table I and plotted in fig. 1 (triangles). This charcoal was exceptional, in that far larger amounts of carbon dioxide were given off during the sorption process than in other cases. To this fact, we ascribe the very considerable "drift" which was observed.|| To eliminate this gas, repeated preliminary charging with water vapour at 10^{-1} mm. pressure, followed by "annealing" at 90° C., was necessary. When finally the carbon dioxide pressure had fallen to 10^{-4} mm., the isothermal became reversible, or, at all events, apparently so.

Table I.

Point.	$p \times 10^2$ in mm.	q in mg./gram.	Point.	$p \times 10^2$ in mm.	q in mg./gram.
1	6.80	2.80	7	0.29	3.57
2	1.30	2.15	8	9.77	5.14
3	9.13	3.98	9	2.98	4.43
4	2.63	3.61	10	6.70	5.02
5	7.78	4.72	11	1.67	3.99
6	11.15	5.17	12	9.28	5.17

Charcoal B.—In this case, when the unextracted charcoal was used, drift occurred to an extent even greater than that observed with charcoal A. As the carbon dioxide pressures found in the vapour phase were always low, it seemed highly probable that the phenomenon was merely due to the absorption of water vapour by some hygroscopic constituent of the ash.¶ A six-point isothermal was therefore determined on a specimen of the charcoal which had been extracted with HCl and water, with a consequent reduction in ash content

* Campbell, 'Proc. Phys. Soc.,' vol. 33, p. 287 (1921).

† 'J. Phys. Chem.,' vol. 32, p. 452 (1928).

‡ 'J. Soc. Chem. Ind.,' vol. 47, p. 376 T (1928).

§ 'J. Phys. Chem.,' vol. 34, p. 2202 (1930).

|| Cf. 'Proc. Roy. Soc.,' A, vol. 129, p. 263 (1930).

¶ This charcoal has been chemically activated by the use of zinc chloride.

from 3.90 to 0.12 per cent.* Reversible results were at once obtained (fig. 1, squares).

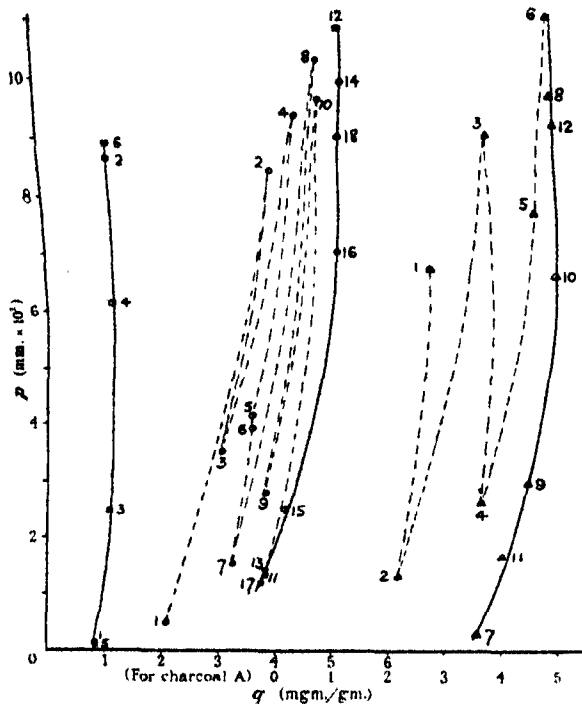


FIG. 1.

Charcoal C.—Two experiments were carried out. In the first, the initial reading was taken at 1.194×10^{-1} mm. and 8.9 mg./gram. Three desorption points followed and then, successively, three sorption points, four desorption points and a sorption point (No. 12; 7.71×10^{-2} mm. and 8.45 mg./gram). Finally, the charcoal was desorbed until q had fallen to 3.28 mg./gram, and the equilibrium pressures read at 53° and 85° C. Plotting these two figures in the form of $\log p$ against $1/T$, and extrapolating the straight line drawn through the two points to a value of $1/T = 1/298$, the derived pressure for 25° C. was found to be 3.1×10^{-4} mm. (point 13). The results are plotted in fig. 2 (triangles). In the second experiment the first reading was taken at the low pressure of 3×10^{-3} mm. and a q value of 2.31 mg./gram. There followed three sorption points, four desorption points and a further number of sorption and desorption points, finishing with No. 20 (9.1×10^{-3} mm. and 4.00 mg./gram). The results are plotted in fig. 2 (squares).

* 'J. Phys. Chem.,' vol. 32, p. 453 (1928).

Some drift was shown by the early points in both experiments, but was distinctly less marked than with charcoal A. In agreement with this fact,

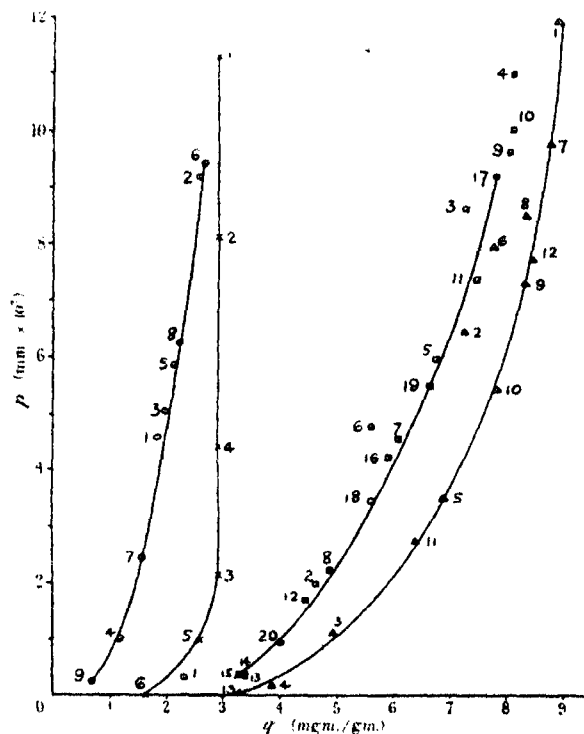


FIG. 2.

the carbon dioxide pressures measured after the first points were low—of the order of 10^{-4} mm. The very slight displacement of carbon dioxide involved was nevertheless probably affecting the nature of the isothermal (*e.g.*, points 8 and 9 of the first experiment). The concordance between the isothermals obtained in the two cases is quite as good as would be anticipated in work involving water vapour.*

It should be added that, in connection with points 1 and 11 of the first experiment, as well as with point 13, readings were taken at more than one temperature which, when plotted in the form of $\log p/T^{-1}$, allowed of a rough calculation of the heat of adsorption. The figures found were as follows:—

* Cf. 'J. Phys. Chem.,' vol. 33, pp. 1682, 1693 (1929).

Table II.

q (mg./gram).	λ (cals./mol.).
8.9	11.4
6.37	14.5
3.28	17.4

Charcoal H.—A nine-point isothermal was determined and is plotted in fig. 2 (circles). Carbon dioxide pressures were of the order of 10^{-4} mm., and any initial drift was insignificant.

Charcoal K.—Measurements with unextracted samples showed the same type of behaviour as was noted with charcoal B, but to an even greater extent, i.e., very pronounced drift, accompanied by very small displacement of carbon dioxide. Charcoal K contains 27.1 per cent. of ash and, as its preparation involves activation with phosphoric acid, it was to be anticipated that, like charcoal B, it might well contain hygroscopic material. A specimen was accordingly extracted with hot distilled water (repeated changes) for several weeks, at the end of which the loss of soluble (acid) material had become very slow and the ash content had been reduced to 24.7 per cent. An isothermal carried out on the extracted material showed initial drift, but far less than before, and seemed to have become reversible after point 11 (fig. 1, circles).

In order to see whether repeated treatment with water vapour would lead to a definitive isothermal with the unextracted charcoal, another experiment was done with this material, in which 41 alternate sorption and desorption points were determined. The drift was, however, still pronounced when the experiment was broken off, the q value at 6×10^{-2} mm. being nearly 13 mg./gram, as compared with 5 mg./gram for the extracted charcoal. It should be added that the slopes of the isothermals above 1×10^{-2} mm. were practically the same in the two experiments, indicating the water taken up by the hygroscopic inorganic constituents to be tightly bound at very low pressures.

Charcoal L.—A six-point isothermal was determined, and is shown in fig. 2. (crosses). It is seen to be of a remarkable nature, no detectible loss or gain of water occurring when the pressure was varied between the limits of 2.1×10^{-2} and 11.3×10^{-2} mm. At the final desorption point (No. 6), the pressure at 25° was below the limit of detection by the Pirani gauge. Carbon dioxide pressures once again were of the order of 10^{-4} mm.

Discussion.

More material is required before the low pressure isothermals of water vapour on charcoal can be fully discussed, and a few points only will be mentioned.

(a) Previous experiments have shown that the general shape of water vapour isothermals on charcoal, at 25°C. and *below a few millimetres pressure* (2–7 mm. depending on the charcoal and the experimental conditions), resembles that of the isothermals of other vapours, such as carbon tetrachloride, *considered over their whole pressure range up to saturation*; Henry's law is not obeyed, but there is relatively greater adsorption at low pressures. This conclusion is now seen to hold equally for the pressure range of approximately 10^{-1} down to 10^{-3} mm. The Henry's law region, if existent, must lie at still lower pressures.

(b) The rate of change of slope of the isothermals at low pressures is in some cases (*e.g.*, charcoals B and L) singularly abrupt.

(c) The behaviour of charcoal A is similar to its behaviour at higher pressures on repeated sorption and desorption.* When the former experiments were done, the dependence of drift on traces of gases still held by the charcoal surface† was not realised.

(d) The quantities of water tightly held at 25° by charcoals A, B and C (say 3·3·5, 0·75 and 2·5–3 mg./gram respectively) are less than the corresponding amounts held after experiments in which higher charging pressures were used.‡ In the latter experiments, the charcoals were initially degassed at higher temperatures (270° or 800° C.), and it is probable that both factors play a part, but that the difference in charging pressure is the more important of the two. We imagine that adsorbed water vapour is less effective than other adsorbed vapours in the matter of freeing a charcoal surface from its residual layer of bound oxygen or adsorbed carbon dioxide.

(e) The conditions of the experimental work were not suitable for determining whether or not breaks§ occur in the water-vapour isothermals of activated charcoals in the pressure range investigated. The relative positions of points 9, 10 and 17 in the second experiment done with charcoal C (fig. 2, squares) suggests such a possibility.

(f) It is of interest to note that the heat of adsorption of water vapour, as

* 'J. Phys. Chem.,' vol. 33, pp. 1701 ff. (1929).

† 'Proc. Roy. Soc.,' A, vol. 129, p. 263 (1930).

‡ 'J. Phys. Chem.,' vol. 33, p. 1710 (1929).

§ 'Proc. Roy. Soc.,' A, vol. 129, p. 246 (1930).

in the case of carbon tetrachloride,* rises with decrease in the quantity sorbed, The values found with charcoal A for pressures of 3 mm. and over (at 25°) were not much different from the latent heat of condensation of the vapour to liquid water.†

Summary.

1. The adsorption of water vapour at 25° C. over a pressure range of 10^{-1} to 10^{-3} mm. has been measured for six different specimens of activated charcoals.
2. The final isothermals obtained were apparently reversible.
3. Further evidence was found respecting the effects exerted by traces of residual gas present on the charcoal surface on the nature of the isothermal.
4. The results of the measurements are briefly discussed.

The work described in this paper was done during 1928. The first experiment on charcoal C was carried out by Dr. R. Chaplin, to whom we wish to make due acknowledgment.

The Emission of Electrons under the Influence of Chemical Action at Lower Gas Pressures.

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§ 1. The work to be described is a continuation of the experiments dealt with in the papers listed in the footnote.‡ For brevity, these papers will be referred to in the sequel by the corresponding numbers. It may be recalled that the results of (5) exhibited a conflict with those of the earlier papers of which (3) is the most important. In the range of partial pressure of COCl_2 used in (5), which extended from about 0.05 to 0.001 mm. of mercury, the electron currents were found to be independent of that pressure; whereas in the earlier experiments, which employed smaller currents, these had been

* 'Proc. Roy. Soc.,' A, vol. 129, p. 252 (1930).

† 'J. Phys. Chem.,' vol. 33, p. 1692 (1929).

‡ (1) Richardson, "Emission of Electricity from Hot Bodies," 1st ed., p. 293 (1916).

(2) Richardson, *loc. cit.*, 2nd ed., p. 310 (1921).

(3) Richardson, 'Phil. Trans.' A, vol. 222, p. 1 (1921).

(4) Brotherton, 'Proc. Roy. Soc.,' A, vol. 105, p. 468 (1924).

(5) Richardson and Brotherton, 'Proc. Roy. Soc.,' A, vol. 115, p. 20 (1927).

varied by controlling the rate of evaporation of the source of COCl_2 , which was kept in a bath of liquid air. In addition, some 50 determinations of the apparent temperature of the emitted electrons in the range of pressure 0.001 to 0.01 mm., as deduced from the energy distribution data, gave values none of which differed by as much as 5 per cent. from 2368°K. , whereas in the earlier work values in the neighbourhood of about 3300°K. , which were thought to be accurate to about 10 per cent., had been obtained. In the earlier experiments, the pressures used were not known, but were thought to be much lower than those in (5). The present experiments have been carried to much lower pressures, with the result that satisfactory progress has been made towards the removal of the discrepancies referred to.

Considerable difficulties were experienced before we could get controllable and measurable pressures of COCl_2 down to 10^{-5} mm. A few of the more important will be mentioned. The same method as in (5) was used, namely, diffusion from a large volume through a capillary tube into the reaction chamber which was exhausted continuously by a Gaede mercury pump. The testing chamber and adjacent parts of the apparatus are shown in fig. 1. The alloy,

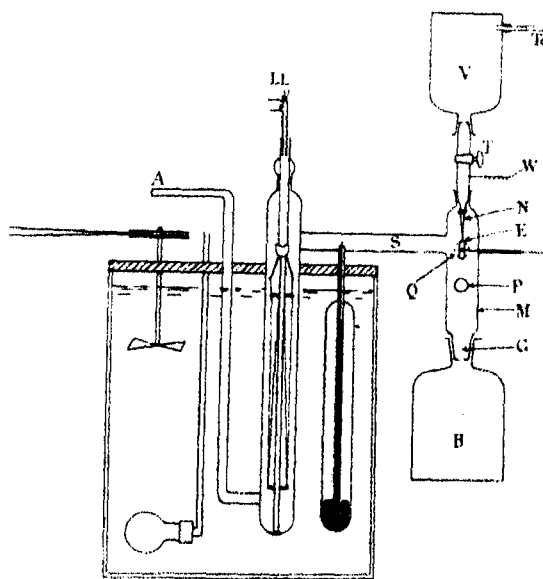


FIG. 1.

which had the composition NaK in all the experiments described in this paper, was stored under an atmosphere of CO_2 in the inverted glass bottle V. By turning the tap T, it flowed through the connecting tube which was ground

into the glass vessels V and M, and fell in drops from the end of the glass nozzle N. This was attached to the connecting tube by a small quantity of sealing-wax, so that different nozzles could be easily interchanged. The orifice of the nozzle N was at the centre of a copper cylinder E, in which a pair of small, circular holes were cut, so that the drops could be illuminated by monochromatic light from a mercury lamp focused on it through the quartz window which terminated the side tube Q. The rate of flow of the drops could be regulated by varying the pressure of the CO_2 in V. Provided that the glass traversed by the alloy was scrupulously clean and that the other conditions were not varied, it was found that the number of drops per minute was exactly proportional to the driving pressure, provided the number did not exceed a certain limit. In the experiments, the number was always kept below this limit, except when the contrary is specifically mentioned. The drops of alloy could be maintained at various potentials by the sealed-in wire W and the electron currents measured by a sensitive electrometer connected to the wire supporting E, shown projecting on the right. The used alloy collected in the ground-in glass bottle B and the side tube P led to the pumping system. The COCl_2 flowed into this system at A through a capillary tube (not shown) 0.06 mm. diameter, of the kind used for squirting cellulose thread, from the large volume made up of a number of glass globes having a total capacity of several litres. It was admitted to this from a small side tube where it was stored in a liquid air bath. The pressure of the COCl_2 in the large volume could be read by two McLeod gauges having different ranges, and a sulphuric acid manometer was also used as a rough indicator of the pressure.

The pressure of the gas in the reaction chamber was measured by the Pirani gauge LL into which it streamed through A and out through the wide tube S. The adaptation of this instrument to measure pressures of COCl_2 down to 10^{-5} mm. has required a separate research and will be described by one of us (L. G. G.) elsewhere. The gauge used consisted of a length of tungsten filament spot-welded to the leads and firmly supported on a glass frame by the system of hooks shown. It was kept in a water bath maintained by a thermostat at $31.0 \pm 0.02^\circ \text{C}$. Actually a water-tight box (not shown) intervened between it and the bath to prevent explosions due to access of water in the event of accidental breakage. This thermostatic control is essential and is what limits the accuracy of the instrument when used for measuring pressure differences.

Much trouble was experienced initially by bursts of gas coming through the nozzle with the alloy. This was ultimately found to be gas generated in the alloy and was got rid of by heating the alloy at 200°C . in a "Monax" glass

vessel, with the pumps working, until evolution of gas ceased and eventually pouring it into the bottle V without letting air have access to it. This process usually required 4 or 5 hours' heating.

The Pirani gauge was placed in one arm of a Wheatstone bridge, the other three arms consisting of fixed constantan coils having resistances of 100·5, 102 and 102 ohms respectively. Campbell's* method of using the gauge was adopted. In this, the resistance and therefore the temperature of the filament is kept constant by adjusting the potential V across the bridge. If V_0 is the balancing voltage for a perfect vacuum and V the voltage required for a balance at pressure p then

$$(V^2 - V_0^2)/V_0^2 = kp, \quad (1)$$

where k is a constant depending on the nature of the gas and on the materials and construction of the gauge. The resistance of the gauge when cold was about 65 ohms and a balance was obtained at 100·5 ohms, so that its working temperature was about 109° C. above room temperature, that is to say, about 125° C.

The Pirani gauge was calibrated by direct comparison with a MacLeod gauge, over a range from about 6×10^{-2} to nearly 10^{-4} mm., for air free from mercury vapour as well as for air and also for COCl_2 each mixed with the mercury vapour and residual gases from the MacLeod gauge and the Gaede mercury pump. It was intended originally to use charcoal immersed in liquid air as the means of evacuation in the final experiments. It was found, however, that the calibration curves for air and for air + mercury vapour were not parallel but always intersected. This showed that the mercury vapour acted not merely as so much additional gas, but that it also affected the Pirani gauge in some other way which we do not fully understand. As there was no means of ascertaining to what extent this effect occurred when COCl_2 was also present, this method of evacuation was abandoned, and in all the experiments described in this paper the evacuation was carried out by the Gaede mercury pump, which was run at a constant speed. We have abundant evidence that the small amount of indifferent residual gas (up to about 0·001 mm.) present under these conditions has no appreciable effect on the phenomena to be described, even though it be many times greater than the partial pressure of the COCl_2 itself. We met with a lot of trouble arising from various causes before we got the apparatus into a condition when the Pirani gauge always gave the same reading for a given reading of the MacLeod gauge, but this condition was attained ultimately.

* 'Proc. Phys. Soc.,' vol. 33, p. 289 (1921).

Operated in the manner just described, the Pirani gauge was not sufficiently sensitive at pressures below about 10^{-4} mm. because the potential across the Wheatstone net could only be read to 0.01 volt, which corresponded roughly to a pressure change of this amount. To go down to partial pressures as low as 10^{-5} mm., the following slightly different method of using the gauge was therefore adopted. A balance was obtained at the lowest pressure attainable by the Gaede pump and the resistance in the battery circuit was not altered during the remainder of the test, *i.e.*, the voltage on the net was kept constant. All pressure differences were then determined from the out-of-balance currents which were set up in the bridge-galvanometer. By this means the requisite sensitiveness was easily obtained. The pressures corresponding to these deflections were ascertained by (1) direct comparison with the deflection caused by a definite reduction of pressure as measured on the MacLeod gauge, and (2) by finding the deflection caused by a small change of voltage at a given low pressure and combining this with the change of pressure for the same change of voltage at a corresponding low pressure extrapolated from the calibration curve obtained for the range of higher pressures as already described. The two methods were found to be in satisfactory agreement. For this method to be satisfactory batteries giving a very constant voltage are required.

The first few trials at these low pressures showed that the variations of the thermostat produced small currents through the galvanometer comparable in magnitude with those caused by the pressure increments, and also that several minutes were required for the establishment of equilibrium after COCl_2 had been admitted. In order that these factors might be taken into account, the deflection of the galvanometer was read every half-minute while the entire apparatus was being pumped out, with the reservoir cut off. When exhaustion had proceeded to its limit (which was indicated by the galvanometer readings fluctuating between fixed values), the reservoir was opened up to the test chamber, and the movements of the needle again followed up by half-minute observations. A typical set of such observations is represented graphically in fig. 2. The humps and hollows on the curve correspond to the periodic heating and cooling of the "constant" temperature bath ($\pm 0.02^\circ \text{C.}$). The horizontal lines represent the mean readings of the galvanometer under the various pressure conditions. By proceeding in this way, the relation between the pressure of COCl_2 in the reservoir and its partial pressure in the test chamber with the Gaede pump running at a constant speed was ascertained for a range of partial pressures from 0.004 to 0.00001 mm., the measurements actually extending to below 0.00004 mm.

The partial pressures (or changes in partial pressure) measured in these experiments are not the same as those at the surface of the drops of alloy in

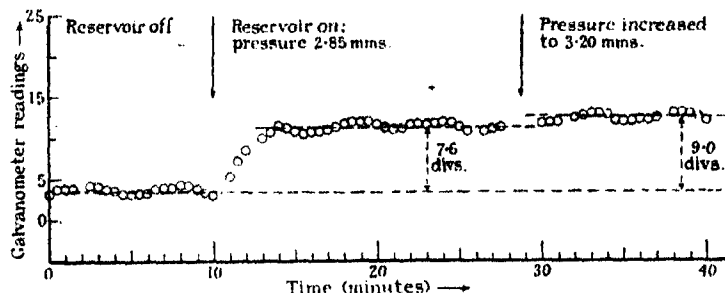


FIG. 2.

the electron emission experiments, for two reasons. In the first place, all the measurements are made in a flow of gas, so that the pressure at the nozzle where the drops form is always less than that indicated by the Pirani gauge. The gradient of pressure from the gauge to the nozzle was made as small as possible by employing a wide connecting tube 2 cm. in diameter.

The second source of uncertainty, and the more important, arises from the presence of the sodium potassium alloy itself, which apparently soaks up the COCl_2 , causing an immediate reduction of pressure. For example, in a particular experiment, when the rate of drops increased from 1 in 10.9 seconds to 1 in 4.68 seconds, the Pirani gauge reading altered from 10.28 volts to 10.20 volts which, on this particular day, corresponded to a pressure change from 6.26×10^{-3} to 5.26×10^{-3} mm.; so that doubling the alloy flow, roughly, reduced the pressure about one-sixth. This effect made it difficult to say exactly how the Pirani gauge readings were related to the pressure at the nozzle. Although the dependence of COCl_2 pressures upon alloy flow was noticed only at pressures higher than 0.001 mm., it was inferred that absorption took place at all pressures to a greater or less extent. In any event, the curve which was drawn between the pressures of the gas in the reservoir as ordinates and the partial pressures of the COCl_2 in the test chamber as abscissæ may be regarded as fixing, for each reservoir pressure, an upper limit to the partial pressure of the COCl_2 which could exist in the test chamber. The slower the alloy entered the more nearly would this limiting value be approached.

Amongst this uncertainty, however, one thing stood out fixed and definite: the input of COCl_2 (mass diffusing through per second), depended only on the reservoir pressure, and was unaffected by the fluctuations of pressure occasioned by the alloy, since the total pressure in the reaction chamber was but a minute

fraction of the driving pressure in the reservoir. As it is probable that at very low pressures all the COCl_2 diffusing into the apparatus is absorbed by, or reacts with, the alloy, it appeared that there might be some advantage, for purposes of comparison, in dealing with input of COCl_2 rather than with reaction pressures. Accordingly, the rate at which phosgene streamed through the capillary was determined as a function of the reservoir pressure, by observing with the Pirani gauge the rate of increase of pressure in the evacuated apparatus when isolated from the pump, and a new curve constructed between reservoir pressure and input. The mass of gas dM/dt entering per second was deduced from

$$\frac{dM}{dt} = \frac{D}{760} v \frac{dp}{dt} \text{ gm. per second,} \quad (2)$$

where D = density of COCl_2 at N.T.P. in gm. per litre, v = volume of apparatus in litres, and dp/dt = rate of increase of pressure in millimetres per second.

After all these calibrations had been made no further changes were made in the apparatus, and checks from time to time showed that the results were valid throughout the remaining experiments.

A search was made for a suitable solvent for removing the traces of sodium potassium alloy which adhered to the apparatus after use. It was very desirable that the glasswork should not be broken during cleaning out, as all the partial pressure measurements had been carried out with the one particular apparatus, and would not apply to another of different shape. It is worth recording that a mixture of equal volume of alcohol and carbon tetrachloride (CCl_4) furnishes a mild, non-inflammable and efficacious cleansing agent,* the use of which has preserved intact the original apparatus after more than a year's service.

Up to the present we have not been able to control in any satisfactory way the hysteresis effects referred to in (1)–(5). We believe that these are due to the presence of a thin, possibly monomolecular, layer of alkaline chlorides which forms on the cylindrical electrode in the test chamber as a result of the action of the COCl_2 on the alkali metal vapour condensed on it. The formation of thin layers of alkali metals on other metallic electrodes by deposition of the atoms which evaporate from the alkali metals in vacuum tubes is a well-

* A word of warning is necessary in this connection ; on one occasion a violent explosion took place whilst cleaning the alloy from a glass vessel with CCl_4 alone. It is possible that there may have been some impurities in this sample of CCl_4 which may have started this reaction.

recognised phenomenon in the field of thermionics. The layer of salt subsequently formed would be expected to be a good insulator when sufficiently dry and the hysteresis effects referred to are of the character to be expected if the outer electrode were covered with a very thin layer of such insulating material. Up to the present the main attack has been concentrated on the observation and measurement of the total current emitted by the alloy under various conditions, as the conditions which give rise to the hysteresis effects are not a serious obstacle in dealing with the saturation currents.

The preliminary procedure was practically the same throughout the whole set of experiments and the following description is applicable to all of them. After the degassed alloy had been mounted in position, the whole of the apparatus (test chamber, MacLeod gauges, reservoir and the COCl_2 supply tube with the COCl_2 frozen in liquid air) was exhausted to the limit of the Gaede pump, *i.e.*, to between 10^{-3} and 10^{-4} mm. of mercury. The Pirani gauge was set working, with the thermostat always at $31.0 \pm 0.02^\circ \text{C}$. and a saturating potential of about — 16 volts was applied to the alloy. The evacuated reservoir was cut off from the pumping connection. Then, provided the Pirani gauge indicated that the leaks in the test chamber were not greater than about 10^{-5} mm. per minute, the tap was opened to admit the alloy, and a small driving pressure of CO_2 was applied to force it through the nozzle. Generally, the alloy flowed very erratically for some time after it was introduced; an interval of half an hour or so was allowed to elapse before attempting to take any readings.

After the apparatus had been used with phosgene in the test chamber for some time, it was found that there was a small negative emission from the drops even when the supply of COCl_2 was cut off and the pump was working. These small currents, which are of the order of 5×10^{-13} amp., have the following properties:—They may be remarkably constant in time. In one particular instance, this emission diminished no more than 5 per cent. during 3 hours' evacuation. They are not photoelectric, for they are not changed when the apparatus is plunged into total darkness. They are not thermionic, for they consist of a stream of electrons with a velocity distribution corresponding to a very high average energy of the type which characterises the chemical effect. The emission is reduced by a single rinsing out with air or CO_2 , but comes back again slowly on re-evacuation. It can be completely got rid of by repeated washing out with CO_2 and subsequent evacuation.

There can be no reasonable doubt that this "stray" emission, as it is convenient to call it, is due to the chemical action of COCl_2 which gets dissolved

in the wax and tap grease present in the apparatus and is afterwards slowly liberated. The experiments to be described later show that the pressure of COCl_2 required to set up, with this particular alloy NaK, a current of 5×10^{-13} amp. is only about 5×10^{-7} mm. of mercury. In carrying out the experiments, the magnitude of these "strays" was noted, so that a correction for them could be made afterwards, if desired.

The following improvement has been made in the method of measuring the various currents:—It was noticed that, with rather slow drops of the kind which it was desired to use, the consecutive determinations of the current under given conditions might differ by as much as 10 per cent. The reason for this is that the current from a drop depends on the surface exposed to the action of the gas, and the surface steadily increases from the moment the drop begins to form. The measured values of the emission could not, therefore, be expected to tally unless observations were made at corresponding instants of a drop's growth, or, alternatively, averaged over many drops. The latter was impracticable for any but the quickest rates of flow, so the plan of dealing with single drops was adopted. On the instant that a drop was observed to detach itself from the nozzle, the electrometer was insulated, and the stop watch started; when the next drop fell off, the electrometer was disconnected from the electrode, which was still insulated, and the watch stopped. The total charge emitted by one drop could then be read at leisure on the electrometer scale. The back electromotive force on the electrode was kept small compared with the saturating potential by using large capacities in parallel with the electrometer.

This mode of observation permitted an accuracy of about 1 per cent., which has proved advantageous for detecting slight variations in saturation currents, such as occur when the alloy flow is altered. It possessed also the great advantage of recording the time of each individual drop; any sudden change in the flow of alloy was immediately made evident.

To sum up the practical side, then, first the magnitude of the "strays" was noted, after which gas was admitted to the reservoir, at a known pressure, and the saturation emission appropriate to this reservoir pressure measured by the method of single drops. The rate of flow of alloy was varied by adjusting the driving pressure of CO_2 , and the effect on the currents studied. The reservoir pressure would then be increased, and the whole of these measurements repeated. In general, the partial pressure or input of COCl_2 in the reaction chamber was inferred from the previously ascertained relations between these quantities and the driving pressure in the reservoir, but the Pirani and MacLeod

gauge readings were taken at frequent intervals to check the pressure conditions. As has been mentioned, after a change in the reservoir pressure it is necessary to wait some minutes until equilibrium is established in the reaction chamber (see fig. 2). In addition to the very small "stray" emissions described above which were due to COCl_2 diffusing out of the tap grease, etc., and which decayed very slowly with time, others of much larger magnitude were frequently present. These were caused by quantities of COCl_2 free in the apparatus, usually the residue from the previous day's experiment, which was quickly cleaned up by the first rush of alloy. For these two reasons the first few readings taken after turning on the reservoir and alloy were sometimes of doubtful significance.

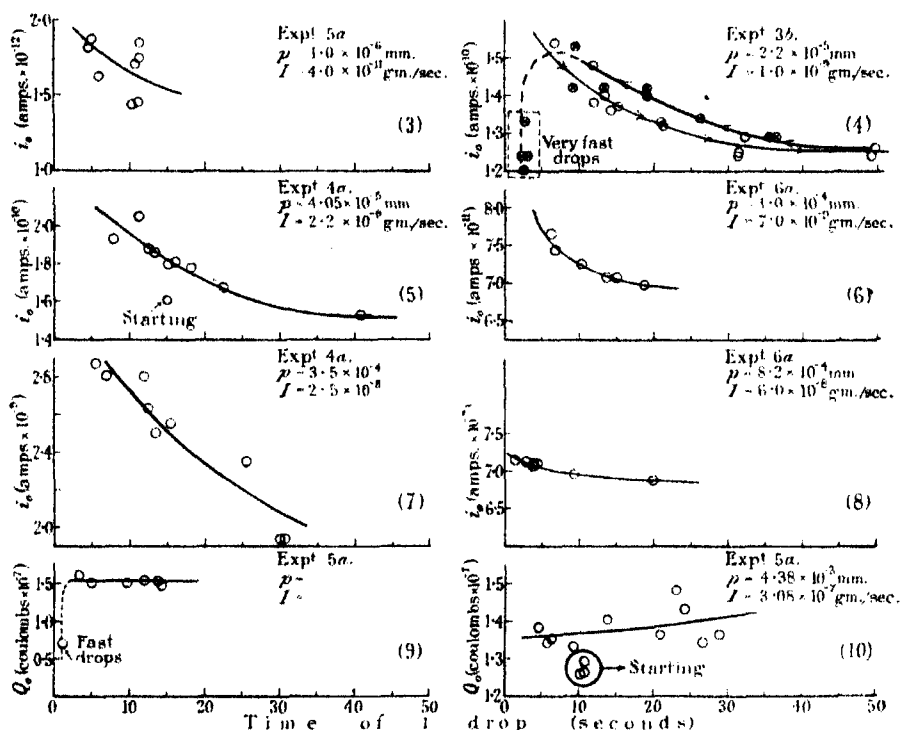
The saturation current depended on the size of the drops; for rates of flow slower than 12 drops per minute the drops appeared to be all about the same diameter, viz., 4 to 5 mm. If, however, the alloy was speeded up by increasing the pressure of CO_2 , a certain rate was reached for which the diameter of the drops suddenly became quite small, and if the driving pressure were further increased the alloy issued as a thin, unbroken stream about $\frac{1}{2}$ mm. in diameter, the diminution of size being accompanied by a sharp decrease in the saturation current. The critical speed at which this change set in depended upon the particular nozzle in use at the time, but usually lay between 15 and 40 drops per minute.

§ 2. *The Emission as a Function of the Rate of the Drops at Different Pressures.*

Typical data showing the emission plotted against the time of one drop at different pressures are exhibited in figs. 3 to 10. In interpreting these, consideration must be paid to the various matters affecting the experiments which have just been discussed. In the different experiments, the time of one drop ranged from about 2 to about 50 seconds, but the principal interest lies in the phenomena shown by the drops for which the time is not less than 5 seconds. These data cover a range of reservoir pressures of COCl_2 from 0.025 mm. to 22.8 mm., the corresponding range of maximum partial pressure in the testing chamber (in the absence of alloy) being 10^{-6} to 4.4×10^{-3} mm. and of COCl_2 input from 4×10^{-11} to 3×10^{-7} gm. per second. For convenience of reference the experiments have been numbered 1a, 1b, 1c, 2a, 2b, 2c, etc., meaning that three investigations were made with the one nozzle No. 1 on successive occasions a, b, c, and so forth.

At the lowest pressures, as in fig. 3, the distribution of the experimental points

exhibit considerable irregularity. This is due to the fact that the currents are so small that the effects of strays are now serious and probably also there



FIGS. 3-10.— i_s = mean saturation current. Q_0 = total change from one drop. p = partial pressure of COCl_2 (in absence of alloy). I = input of COCl_2 in gm./sec.

are fluctuations in the pressure in the apparatus at these low pressures. More definite conclusions can be drawn from observations made at an appreciably higher pressure, such as those shown in fig. 4. This figure, in fact, illustrates a number of interesting points, as well as some experimental difficulties, associated with these experiments. It will be seen that the points taken first indicated thus $\odot$ lie on the whole lower than those indicated thus $\otimes$ which were taken later. We interpret this as meaning that there was some accumulation of COCl_2 in the apparatus in the course of this experiment. The currents in fig. 4 for a given rate of drops are also somewhat larger than those found at the same reservoir pressure on the previous day. This suggests that such accumulation had been going on for some time. It is therefore probable that the maximum partial pressure in fig. 4 is underestimated in comparison with other similar cases in which such changes were not found to be occurring.

In any event, fig. 4 clearly demonstrates that the electron current diminishes as the time T of the drops increases from about 5 to 50 seconds. The change produced by varying T from 10 to 50 seconds is not very large, the current i_0 falling from 1.42×10^{-10} to 1.25×10^{-10} amp. For very fast drops it is evident from fig. 4 that i_0 is reduced appreciably. This is, presumably, because the drops get smaller and the conditions are no longer comparable with those obtaining when the slower drops are falling.

An examination of the data incorporated in figs. 3 to 8 and other similar data within the same range of low pressures showed that all the $i_0 - T$ curves were approximately hyperbolic, so that we may put

$$(i_0 - a)(T + b) = k, \quad (3)$$

where a , b and k are constants which depend on the gas pressure.

We now turn to fig. 10, which shows the result of an experiment made at the much higher reservoir pressure of 22.8 mm. In absence of alloy, this would have set up a pressure in the testing chamber of 4.38×10^{-3} mm. The phenomena exhibited at this concentration of gas were in striking contrast to those described above; the currents were now almost directly proportional to the speed of the alloy. This is depicted in fig. 10, where the total charge from one drop is shown to be practically independent of T (which is, of course, only another way of stating the same thing). The appearance of the drops also changed remarkably; instead of a succession of bright, nimble pellets there exuded dull, sluggish, pear-shaped globules, which slithered off the nozzle, often leaving behind them stalactite-like tails of the alloy petrified within a skin of reaction products. Measurements under such conditions could only be of the roughest description. The pressure in the apparatus underwent wild fluctuations the whole time the alloy flowed; the entry of a fresh drop was heralded by a jerk of the Pirani bridge galvanometer. When the natural inertia of the Pirani gauge is taken into consideration, it will be realised that the pressure pulsations which could impart such a lively motion to such a ponderous instrument must have been violent indeed. For these reasons the somewhat irregular distribution of the points exhibited by fig. 10 is not surprising. More consistent results, which demonstrate clearly the independence of the total charge emitted by one drop, of the time of the drop at these high pressures were got in the experiment the results of which are shown in fig. 9. The pressure during this experiment is not known exactly, but it was about the same as that during the observations of fig. 10.

Figs. 3 to 10 do not include the whole of the observational material of this

kind which was obtained. A number of other experiments were made with results which served to confirm the conclusions which have been drawn from the experiments which have been described.

§ 3. *The Emission as a Function of the Gas Pressure for Different Rates of Drops.*

By inter- and extrapolation of all these experimental results a table was drawn up showing the saturation current i_0 as a function of COCl_2 concentration for standard rates of flow of the alloy, namely, for the time T of one drop = 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 seconds. These, together with some other relevant data, are exhibited in Table I. Owing to the large range of variation of saturation currents (i_0) and of partial pressures (p) (roughly 10,000-fold), the data of Table I are best exhibited logarithmically as in fig. 11. The curves with points marked thus: $\circ$, $\blacksquare$, $\bullet$, $\blacktriangle$, $\blacksquare$, $\square$, and $\otimes$ show $\log. i_0$ against $\log. p$ for rates of flow of alloy of 1 drop in 5 (about) 8, 10, 15, 20, 25 and 35 seconds respectively. As has been explained in § 1, p is the limiting partial pressure which would hold if there were no alloy flowing. The curves with points marked thus $\times$ and $+$ show, to the same scale, $\log. i_0$ against $\log. I$ for $T = 5$ and 10 seconds respectively, where I is the input of COCl_2 in gram. per second. The two sets are very similar, which shows that I and p may be considered fairly equivalent measures of the concentration of COCl_2 in the apparatus.

The data for the slower are not so complete as for the faster drops; this was due to the high room temperatures prevailing during these experiments. Often the nozzle offered so little resistance to the flow that the alloy ran out very fast even when the driving pressure of CO_2 had been reduced to zero; the only way of varying the flow under these conditions was to shut off the tap to the testing chamber and allow the column of alloy below to flow out under its own weight, the drops becoming progressively slower as the head of alloy diminished. A nozzle which was quite satisfactory at one temperature was practically useless at a temperature 10°C. higher.

However, fig. 11 proves the following :—

(1) i_0 increases continuously with p from zero up to a critical value in the neighbourhood of $p = 10^{-3}$ mm. Hg. This critical value depends upon the alloy flow; it is smaller, the slower the drops. As p increases beyond the critical point, the saturation currents rapidly approach upper limits, the magnitudes of which are almost exactly inversely proportional to the times of the drops. In other words, the greatest charge emitted by any drop is

Table I.
COCL₂ — NaK; Saturation Currents (in amperes) for various Alloy Flows.

Number of experiment.	Reservoir pressure of COCl ₂ (mm. Hg.)	Partial pressure of COCl ₂ (mm. Hg.)	Input of COCl ₂ (gm./sec.).	Time of one drop in seconds.									
				5.	10.	15.	20.	25.	30.	35.	40.	45.	50.
2c	2.40	1.07 × 10 ⁻⁴	7.6 × 10 ⁻⁹	1.20 × 10 ⁻¹⁰	1.26 × 10 ⁻¹⁰	1.25 × 10 ⁻¹⁰	1.17 × 10 ⁻¹⁰	1.08 × 10 ⁻¹⁰	1.28 × 10 ⁻¹⁰	1.26 × 10 ⁻¹⁰	1.25 × 10 ⁻¹⁰	9.36 × 10 ⁻¹⁰	—
3a	0.61	2.2 × 10 ⁻⁵	1.0 × 10 ⁻⁹	1.20 × 10 ⁻¹⁰	1.42 × 10 ⁻¹⁰	1.38 × 10 ⁻¹⁰	1.54 × 10 ⁻¹⁰	1.50 × 10 ⁻¹⁰	1.50 × 10 ⁻¹⁰	1.30 × 10 ⁻¹⁰	1.25 × 10 ⁻¹⁰	1.25 × 10 ⁻¹⁰	1.25 × 10 ⁻¹⁰
3b	0.61	2.2 × 10 ⁻⁵	1.0 × 10 ⁻⁹	1.52 × 10 ⁻¹⁰	1.50 × 10 ⁻¹⁰	1.44 × 10 ⁻¹⁰	1.40 × 10 ⁻¹⁰	1.58 × 10 ⁻¹⁰	1.82 × 10 ⁻¹⁰	1.30 × 10 ⁻¹⁰	1.28 × 10 ⁻¹⁰	1.27 × 10 ⁻¹⁰	1.26 × 10 ⁻¹⁰
3c	0.61	2.2 × 10 ⁻⁵	1.0 × 10 ⁻⁹	1.58 × 10 ⁻¹⁰	2.00 × 10 ⁻¹⁰	1.80 × 10 ⁻¹⁰	1.60 × 10 ⁻¹⁰	1.50 × 10 ⁻¹⁰	1.40 × 10 ⁻¹⁰	1.40 × 10 ⁻¹⁰	1.34 × 10 ⁻¹⁰	1.31 × 10 ⁻¹⁰	1.29 × 10 ⁻¹⁰
4a	1.05	4.05 × 10 ⁻⁵	2.2 × 10 ⁻⁹	2.08 × 10 ⁻¹⁰	1.94 × 10 ⁻¹⁰	1.82 × 10 ⁻¹⁰	1.73 × 10 ⁻¹⁰	1.66 × 10 ⁻¹⁰	1.61 × 10 ⁻¹⁰	1.56 × 10 ⁻¹⁰	1.53 × 10 ⁻¹⁰	1.51 × 10 ⁻¹⁰	1.50 × 10 ⁻¹⁰
4b	5.43	3.5 × 10 ⁻⁴	2.5 × 10 ⁻⁸	2.96 × 10 ⁻⁹	2.75 × 10 ⁻⁹	2.53 × 10 ⁻⁹	2.35 × 10 ⁻⁹	2.20 × 10 ⁻⁹	2.10 × 10 ⁻⁹	2.00 × 10 ⁻⁹	1.94 × 10 ⁻⁹	1.91 × 10 ⁻⁹	1.89 × 10 ⁻⁹
4c	0.20	8.0 × 10 ⁻⁶	3.0 × 10 ⁻¹⁰	1.05 × 10 ⁻¹⁰	1.02 × 10 ⁻¹⁰	1.00 × 10 ⁻¹⁰	9.9 × 10 ⁻¹¹	4.15 × 10 ⁻¹¹	—	—	—	—	—
4d	0.59	2.0 × 10 ⁻⁵	1.0 × 10 ⁻⁹	2.65 × 10 ⁻¹⁰	2.35 × 10 ⁻¹⁰	2.20 × 10 ⁻¹⁰	2.07 × 10 ⁻¹⁰	2.00 × 10 ⁻¹⁰	—	—	—	—	—
4e	1.13	8.8 × 10 ⁻⁵	6.0 × 10 ⁻⁹	5.20 × 10 ⁻¹⁰	5.20 × 10 ⁻¹⁰	5.20 × 10 ⁻¹⁰	—	—	—	—	—	—	—
4f	3.12	1.52 × 10 ⁻⁴	1.1 × 10 ⁻⁸	1.0 × 10 ⁻⁹	9.56 × 10 ⁻¹⁰	9.56 × 10 ⁻¹⁰	1.12 × 10 ⁻⁹	1.04 × 10 ⁻⁹	—	—	—	—	—
4g	3.82	2.01 × 10 ⁻⁴	1.5 × 10 ⁻⁸	1.0 × 10 ⁻⁹	3.20 × 10 ⁻⁹	3.00 × 10 ⁻⁹	—	—	—	—	—	—	—
4h	5.82	3.9 × 10 ⁻⁴	2.8 × 10 ⁻⁸	1.0 × 10 ⁻⁹	9.5 × 10 ⁻⁹	9.5 × 10 ⁻⁹	—	—	—	—	—	—	—
4i	7.50	5.9 × 10 ⁻⁴	4.16 × 10 ⁻⁸	1.0 × 10 ⁻⁹	1.02 × 10 ⁻¹²	1.54 × 10 ⁻¹²	—	—	—	—	—	—	—
5a	0.025	1.0 × 10 ⁻⁶	4.0 × 10 ⁻¹¹	1.80 × 10 ⁻¹²	1.62 × 10 ⁻¹²	1.62 × 10 ⁻¹²	—	—	—	—	—	—	—
5b	2.80	4.38 × 10 ⁻⁵	3.08 × 10 ⁻⁷	2.7 × 10 ⁻⁸	1.86 × 10 ⁻⁸	9.15 × 10 ⁻⁹	6.9 × 10 ⁻⁹	5.6 × 10 ⁻⁹	4.8 × 10 ⁻⁹	—	—	—	—
5c	2.80	1.0 × 10 ⁻⁴	7.0 × 10 ⁻⁹	8.0 × 10 ⁻¹⁰	7.10 × 10 ⁻¹⁰	6.95 × 10 ⁻¹⁰	6.9 × 10 ⁻¹⁰	—	—	—	—	—	—
5d	3.95	2.12 × 10 ⁻⁴	1.6 × 10 ⁻⁸	1.64 × 10 ⁻⁹	1.58 × 10 ⁻⁹	1.56 × 10 ⁻⁹	1.55 × 10 ⁻⁹	—	—	—	—	—	—
5e	9.20	8.2 × 10 ⁻⁴	6.0 × 10 ⁻⁸	7.05 × 10 ⁻⁹	6.90 × 10 ⁻⁹	6.85 × 10 ⁻⁹	—	—	—	—	—	—	—

Additional Isolated Points.

Number of experiment.	Reservoir pressure of COCl ₂ (mm. Hg.)	Partial pressure of COCl ₂ (mm. Hg.)	Input of COCl ₂ (gm./sec.).	Saturation emission i_0 (amperes) for various times T of one drop.							
				T	i_0	T	i_0	T	i_0	T	i_0
5a	2.05	3.9 × 10 ⁻⁵	6.0 × 10 ⁻⁹	7.7	5.24 × 10 ⁻¹⁰	—	—	—	—	—	—
5b	3.80	2.0 × 10 ⁻⁴	1.5 × 10 ⁻⁸	8.1	1.36 × 10 ⁻⁹	—	—	—	—	—	—
5c	6.40	4.5 × 10 ⁻⁴	3.2 × 10 ⁻⁸	8.1	3.04 × 10 ⁻⁹	—	—	—	—	—	—
5d	11.0	1.11 × 10 ⁻³	8.3 × 10 ⁻⁸	9.3	9.42 × 10 ⁻⁹	—	—	—	—	—	—
5e	19.1	3.23 × 10 ⁻³	2.29 × 10 ⁻⁷	4.15	4.18 × 10 ⁻⁸	5.45	3.40 × 10 ⁻⁸	5.60	3.15 × 10 ⁻⁸	7.73	2.37 × 10 ⁻⁸

independent of T . This conclusion has already been drawn from figs. 9 and 10 which represented observations at the higher pressures.

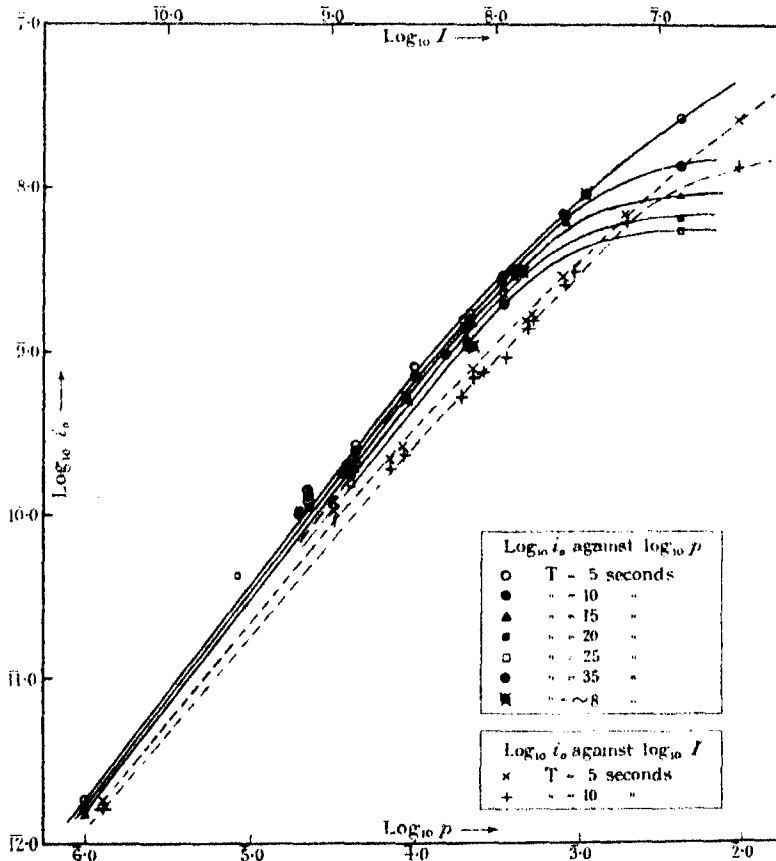


FIG. 11.— T = Time of 1 drop in seconds. i_0 = Saturation emission. p = Partial pressure of COCl_2 in millimetres Hg. I = Input of COCl_2 in gr. per second.

The slopes of both input and partial pressure curves are almost constant for p less than about 10^{-3} mm., and are each a little higher than unity, so that i_0 increases rather more rapidly than it would if it were proportional to p . More precisely, for $0.0005 > p > 0$,

$$i_0 = A \cdot p^{1.3} = B I^{1.27}, \text{ approximately,} \quad (4)$$

where A and B are constants. We also infer that p does not increase quite in proportion to I :

$$p = \left[\frac{B}{A} I^{1.27} \right]^{\frac{1}{1.3}} = C I^{0.977}. \quad (5)$$

We incline, however, to the view that the emission is really proportional to the pressure at low pressures, the apparent deviations being due to the fact that the actual values of the pressure are not known and to other subsidiary causes.

(2) i_0 depends upon T at all pressures ; the intercepts on any line of constant pressure depict the variation of i_0 with T at fixed pressure. Interpreting the data broadly, we may say that at high pressures i_0 is inversely proportional to T , whilst at low values of p , i_0 may be taken as independent of T without serious error, a condition of affairs which it tends to approach exactly, as p tends to zero.

The experimental data were gathered under such a diversity of conditions as regards shape and size of nozzle (which must have decided the diameter of the drops), and its position with respect to the holes in the electrode, that it is difficult to say what the exact shape of the middle parts of the curves in fig. 11 should be. In all probability, were it possible to eradicate the differences which occur from one experiment to another, the curves would be found to diverge continuously in the manner indicated in fig. 12.

It does not assist matters to neglect the composite curves altogether, and

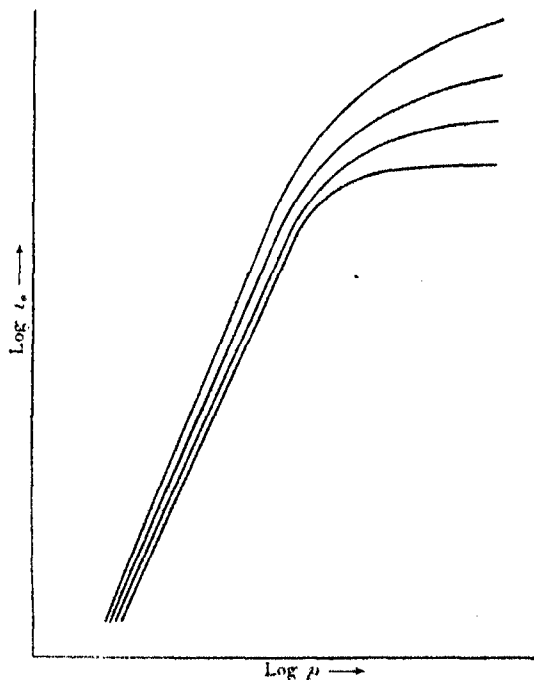


FIG. 12.

deal with the data of separate tests : the table below gives the ratio i_0 ($T = 15$) : i_0 ($T = 5$), for various reservoir pressures P .

Table II.

P (mm.)	0.61	1.05	3.82	3.95	5.43	9.20	22.8
i_0 ($T = 15$) $\leftarrow$ i_0 ($T = 5$) }	0.91	0.87	0.78	0.95	0.83	0.97	0.34

These figures are curiously inconclusive ; the inconsistencies cannot be due merely to errors of measurement.

(3) All the facts are in agreement with the conclusion that the maximum total charge which can be emitted by any one drop is a fixed quantity, which, however, would presumably be proportional to the size of the drop.

It has been observed on many occasions that at high pressures no more charge is given off from a drop after a certain time has elapsed, no matter how long the drops may continue to hang in the gas. The latter part of the life of the drop is unproductive of current, yet this interval is added in for computing the mean current ; for this reason it is somewhat artificial to deal with currents, the more natural way being to deal with charges.

It is not certain whether the cessation of electron emission observed with slow drops at high pressures is due to the cessation of the chemical action or to the formation of a layer of reaction products which is thick enough to absorb all the electrons generated. In any event, this effect of the reaction products must be important. Emission of charge takes place immediately the reaction commences, and as the skin of chlorides thickens, more and more of the slower electrons are prevented from reaching the outer electrode owing to the retarding action of the layer of reaction products, so that we should expect the mean current to depend on the time during which a drop hangs in the gas at all pressures. Naturally, the effect would be very small for low concentrations of active gas, and more noticeable for higher concentrations. Emission would thus proceed until the reaction products had accumulated in sufficient quantity to prevent further emission. No drop could emit more charge than that corresponding to the amount of chemical action which takes place during the building up of the totally arresting layer. This might be true whether the chemical action were arrested at this stage or not. Whether or not a given drop can send off the limiting charge would therefore be decided by the gas pressure and the time during which the drop remains on the nozzle.

The limiting charge for globules of NaK of about 4 mm. diameter appears to be somewhat in the region of 2.0×10^{-7} coulomb. On this view the general features of the variation of i_0 with T at different pressures are at once accounted for.

An idea of the thickness of the totally arresting layer can be got by assuming that every molecule of COCl_2 which impinges on the alloy leaves two molecules of chlorides on it. This estimate will probably be too high, but it should in any event give an upper limit. At the critical pressure $p_0 = 4 \times 10^{-4}$ cm. (of mercury), at which the $\log. i : \log. p$ curve becomes flat for $T = 15$ seconds, the usual kinetic theory formulæ shows that 9.3×10^{18} molecules of COCl_2 would strike unit area of the surface of the drop during this interval. If these were all effective, the layer formed would be about 10^4 molecules deep. This estimate is probably not very far wrong, as it is clear from inspection of the drops in this condition that they are covered with a skin whose thickness is not small compared with the wave-length of light. If each of the molecules of COCl_2 which struck the surface generated an electron, the total possible quantity coming from 9.3×10^{18} molecules would be 4.5×10^9 e.s.u. or 1.5 coulombs. Since the actual electron emission appears to be of the order 2×10^{-7} coulomb, it seems, even when every allowance is made for the factors which reduce the yield, that the emission of an electron is a comparatively infrequent event in the chemical process.

§ 4. *The Distribution of Energy among the Emitted Electrons.*

The additional information which we have obtained about this question is less complete than we should have wished on account of the difficulties raised by the hysteresis effects. What appeared to be two fairly good measurements were obtained, one (3a) at a pressure of COCl_2 about 2.2×10^{-5} mm., and one drop in 14 seconds, and the other (2c) at a pressure of 1.07×10^{-4} mm. and one drop in 44 seconds. It was found impossible to work simultaneously the method of single drops and Townsend's null method (balancing out the back electromotive force on the electrode by passing a charge through a condenser in parallel with the electrometer) referred to in (4) and used also in (5). The null method was therefore abandoned. The back electromotive force was kept as small as possible by using large capacities in parallel with the electrometer. The final potential between electrode and alloy was calculated from the electrometer deflection, which enabled the slope, as defined in (5), to be fixed within narrow limits. The determination (2c) with $p = 1.07 \times 10^{-4}$ mm., $T = 44$, gave a slope of

3.3, the "equivalent temperature" being about 3600°K. , the one (3a) with $p = 2.2 \times 10^{-5}\text{ mm.}$, $T = 14$ seconds, gave a slope of 4.3 the equivalent temperature to which is 2760°K.

In addition to these, a rougher estimate could be got for a much lower pressure by making use of the persistent small stray effect described above. In this experiment, the saturation current was 6.5×10^{-13} amp. which from equation (4) corresponds to a partial pressure $p = 5 \times 10^{-7}\text{ mm.}$ The time of one drop in this experiment was about 47 seconds. The slope of the straight part of the $\sigma V : V$ curve was determined as 2.46, which corresponds to an equivalent temperature of about 4500°K.

It will be convenient here to catalogue the various determinations of these equivalent temperatures which have been made at different times and under different conditions.

(1) In (5) Richardson and Brotherton made 44 determinations at pressures of COCl_2 between 0.001 and 0.01 mm., i_0 between 2.8×10^{-11} and 7.5×10^{-8} amp., T between 1 and 60 and composition of alloy ranging from 50 per cent. K to 90 per cent. K. In none of these did the equivalent temperature $T^{\circ}\text{K.}$ differ by 5 per cent. from the mean value 2368°K.

(2) Experiment (2c) just described in which $p = 1.07 \times 10^{-4}\text{ mm.}$, $T = 44$ and $T^{\circ}\text{K.} = 3600^{\circ}\text{K.}$

(3) Experiment (3a) just described in which $p = 2.2 \times 10^{-5}\text{ mm.}$, $T = 14$ and $T^{\circ}\text{K.} = 2760^{\circ}\text{K.}$

(4) Various determinations in (3) under different conditions of p , T and alloy composition. As judged from the magnitude of the saturation current, the pressure must have been varying considerably throughout a single experiment in many of the determinations. For the two experiments which showed the least variation in the saturation current the values of p as estimated from this quantity were 3×10^{-6} and 5×10^{-6} with a mean value of $4 \times 10^{-6}\text{ mm.}$ The data of these experiments treated in various ways gave a value for $T^{\circ}\text{K.}$ of 3300°K. with an estimated accuracy of about 10 per cent.

(5) The experiment with the "stray" emission for which $p = 5 \times 10^{-7}\text{ mm.}$, $T = 47$ seconds, which gave $T^{\circ}\text{K.} = \text{about } 4500^{\circ}\text{K.}$ On account of the small number of points and the smallness of the currents this determination is, from the point of view of obvious experimental errors, much rougher than the others and might involve an uncertainty of 30 per cent.

The most striking thing about these determinations is that all the values got with $p < 0.001\text{ mm.}$ are appreciably higher than the constant value got by Richardson and Brotherton in (5) for values of p greater than this limit.

It cannot be asserted with confidence that any of these values differ from 3500° K. by an amount which exceeds the possible errors which may be concealed in these experiments. Even at a pressure as low as 5×10^{-7} mm. the measured equivalent temperature has not got above 4500° K., a value which might be reduced owing to obvious experimental inaccuracies to as low as 3500° K. It seems, therefore, rather certain that at low pressures this equivalent temperature settles down at a value which is not very different from that determined in (3). From the present experiments it looks as if most of the rise from 2368° K. to the higher value takes place in the range of pressure just below 0.001 mm. In fact, it seems likely that most of this change is complete by the time the pressure is sufficiently reduced for the straight part of the curves in fig. 11 to be reached. In order to adopt this interpretation, it is necessary to suppose that the experiment No. 3a of this paper is affected by some hysteresis changes, as there is nothing in the way of obvious experimental errors which could raise this determination from 2760° K. to, let us say, 3300° K. We cannot, however, deny the possibility of a hysteresis effect of a magnitude sufficient to have caused such a displacement.

While the exact value of the equivalent temperature of the electrons emitted at the lowest ascertainable pressures is uncertain and must be left for future investigation, the experimental evidence establishes quite definitely that it is a very high temperature of some thousands of degrees. This fact shows that this phenomenon of electron emission is a true characteristic of the chemical action involved and is not a secondary effect arising from thermionic emission due to the rise in temperature caused by the heat generated by the chemical action at the surface of the metal. This statement, or an equivalent one, has been made before, but it does not seem to have carried complete conviction. However, a little reflection on the magnitudes involved will show that the conclusion is correct.

Consider first the maximum average temperature which the drop as a whole can attain. An upper limit for this can be got by assuming that every molecule of COCl_2 which strikes the surface of the drop reacts with it and that all the heat generated at the surface goes into the drop, none being lost by convection or radiation. This amount of heat is $n_0 Q T S$, where n_0 is the number of molecules striking unit area of the drop, whose total area is S , in unit time, Q is the heat of reaction per molecule and T is the time of a drop. Taking Q as the equivalent of 1.9×10^5 gm. calories and dividing by the heat capacity of a typical drop, radius 2 mm. and $T = 15$ seconds, this gives for the upper limit to the average temperature of a drop when the pressure of COCl_2 is

4×10^{-7} mm. 0.025° C. Since the heat is generated at the surface it is clear from this result that the rise in temperature at the centre is a very small quantity compared with 1000° C.

We now calculate an upper limit for the temperature of the surface of the drop. We are only concerned with the order of magnitude of this temperature, not its exact value, so we do not need to bother with the spherical problem. It is sufficient to consider the similar problem of a plane sheet whose thickness is equal to the radius r of the drop. This is subject to the chemical action on one side which is raised to a temperature θ , that of the other side being θ_0 . The maximum value of θ will be given by

$$n_0 Q = \sigma (\theta^4 - \theta_0^4) + \frac{\kappa}{r} (\theta - \theta_0),$$

where σ is the radiation emissivity and κ is the thermal conductivity of the material. This equation assumes that every impinging molecule reacts and neglects any loss due to convection. A consideration of the magnitudes shows that the effect of the radiation term is unimportant and at $p = 4 \times 10^{-7}$ mm. of mercury we find for the upper limit of $\theta - \theta_0$ the value $1.9 \times 10^{-5}^\circ$ C. It is quite evident that the rate of generation of heat at the surface of the drop at these low pressures is too small to cause any appreciable increase of temperature either of the surface of the drop or of the drop as a whole. There is no possibility of a local heating to some thousands of degrees which the thermionic emission idea would require.

This conclusion is valid whether the reaction spreads uniformly over the surface or whether it spreads sideways in patches. A patch must be at least one molecule thick; otherwise it seems to have no meaning. Patches cannot raise the foregoing maximum temperatures, which are deduced on the assumption that every molecule of COCl_2 reaching a given area reacts completely. If the reaction is localised, it cannot proceed anywhere at a greater rate than this; so that the local temperatures cannot be higher than the above values. The opportunity for the heat generated to flow away will, in fact, be somewhat increased, so that the maximum local temperatures will be correspondingly reduced. The whole amount of heat communicated to the drop if the reaction proceeds in patches will also be less than the maximum amount calculated above, since only a fraction of the molecules of COCl_2 which strike the drop will react with it under this mechanism.

We are glad to have this opportunity to express our indebtedness to the Government Grant Committee for a grant to one of us (O. W. R.) and to the

Department of Scientific and Industrial Research for a grant to the other (L. G. G.). Without these grants it would have been impossible for us to have carried this work to its present stage.

Summary.

A method is described by which partial pressures of phosgene can be controlled and their changes measured down to 10^{-5} mm. Hg. The electron emission from NaK in this gas has been measured down to directly measured pressures of 10^{-5} and to extrapolated pressures of 5×10^{-7} mm. under various conditions. In contrast to the results at pressures above 10^{-3} mm., the emission is now found to be a function of the gas pressure as Richardson originally supposed. This function is determined by the experiments. Evidence is also brought forward to show that the experimentally determined velocity distribution function among the electrons approaches a limit as the pressure is reduced.

*Address of the President, Sir Ernest Rutherford, O.M., at the
Anniversary Meeting, December 1, 1930.*

At this, our Annual Meeting, we are naturally conscious of the severe losses in our ranks in the course of the year. We have to deplore the removal by death of some of the best known and most valued Fellows, including Lord Balfour and Sir William McCormick, elected under Statute 12, Professor Le Bel, Foreign Member, and twelve Fellows of the Society.

The death of the EARL OF BALFOUR at the age of 82 removed from our midst a public figure of the first magnitude. Although Balfour's activities covered a wide field, and although through a great part of his career he carried heavy responsibilities in guiding the affairs of the Nation, science was always with him a topic of primary interest. If he cannot be said to have made original contributions to scientific knowledge himself, there can be no doubt that his championship of the cause of science was of the greatest indirect benefit. As First Lord of the Treasury in 1900, he did much to help forward the scheme for the National Physical Laboratory, in which his brother-in-law, Lord Rayleigh was interesting himself. He was constantly called upon to preside, or to speak, at meetings for the furtherance of scientific objects, or the commemoration of the great scientific careers of the past, and seldom failed to add distinction to such occasions. He may indeed be regarded as a chief interpreter of science to the English public during his generation. He was President of the British Association at Cambridge in 1904. He was elected to the Royal Society under Statute 12, as early as 1888, at the age of 40 years. He served on the Council in 1907-08 and again in 1912-14. But, perhaps, his chief work for science was in his later years, after the most active part of his political career was over. In two successive terms of office as Lord President of the Council, he was the Minister responsible for the Department of Scientific and Industrial Research, and for the Medical Research Council. Of the latter body he acted as chairman until the onset of his illness. He watched the scientific interests under these departments with close personal attention, and did much to establish them on a permanent basis. Finally, to him was due the Committee of Civil Research,

complementary to his older creation of the Committee of Imperial Defence. He was Chancellor of the Universities of Cambridge and Edinburgh, and President of the British Academy. His is a place which will not easily be filled.

Sir WILLIAM MCCORMICK, who died suddenly in his seventy-first year, had a very varied career of service to the Universities and to the State in many capacities. At one time Professor of English in University College, Dundee, he became the first Secretary of the Carnegie Trust for the Universities of Scotland. He was for many years Chairman of the University Grants Committee where his personal influence and advocacy were largely instrumental in obtaining the increased grants for the Universities in the difficult post-war period. He was the first Chairman of the Advisory Council of the Department of Scientific and Industrial Research which was set up in 1916 under the pressure of the war to organise the application of science to industry. The success of this Department, which is known to you all, was in no small part due to his financial acumen and organising ability. Although not trained as a scientific man, he had a wide interest in science and sympathy with the scientific outlook and worked loyally with his band of scientific advisors—originally all Fellows of our Society. The Society was glad to recognise the value of his services to Science by electing him a Fellow under the special statute. His charm of manner and breadth of outlook endeared him to all his friends, and he will be greatly missed.

The death of Admiral Sir HENRY JACKSON at the age of 75, has caused deep regret in both naval and scientific circles. When in the Navy, in 1891, he began experiments to test the utility of Hertzian waves as a means of communication between ships at sea, and was largely instrumental in the rapid development of this method of signalling in the Navy. As early as 1902, in a paper to our "Proceedings," he drew attention not only to a failing of signals but also to their reappearance as the distance between the signalling and receiving ships increased. During the war, he was appointed as First Sea Lord in 1915 when Lord Fisher left the Admiralty. On his retirement from active service, he was appointed, in 1920, Chairman of the Radio Research Board, instituted by the Department of Scientific and Industrial Research. In this capacity he did admirable work in encouraging researches on the fundamental problems of radio-transmission. He was elected to our Fellowship in 1901 and was awarded the Hughes Medal in 1926. His charm of manner, simplicity of nature and devotion to duty endeared him to all those with whom he came in contact.

IN PERCY ALEXANDER MACMAHON the mathematical world has lost a distinguished and enthusiastic worker of marked individuality, as well as a most attractive personality. An algebraist of great resource and insight, he was early attracted by the theory of invariants (in the most extended sense) and symmetric functions, and his discoveries in connection with the differential operators in these theories gained at once the warm appreciation of the great exponents, Cayley and Sylvester. By a natural sequence he was led on to intricate problems of Combinations and Probability, to which his researches had already opened a line of attack. His work on these subjects was afterwards collected in the two volumes published under the title "Combinatory Analysis," by the Cambridge Press. An interesting by-product of his later years was the theory of repeating patterns, with which he occasionally amused an audience, and which afforded an outlet for his strong sense of humour. He died on Christmas Day 1929, at the age of 75.

DR. SEBASTIAN ZIANI DE FERRANTI who died in January last was the great pioneer of electricity supply at high pressure. He was of Italian descent from one of the Doges of Venice, but was educated and lived all his life in England. At the age of eighteen, he patented the Ferranti alternator and a few years later, while still a young man, designed a system of supply from Deptford which was transmitted at 10,000 volts. Little was then known about these high pressures and no instruments for measuring them were in existence. Ferranti consulted Lord Kelvin on some abstruse points in mathematical physics during the course of his work. In 1892, he severed his connection with supply and started the firm of Ferranti, Ltd., which manufactured many of the machines and devices he had perfected. He was careful to make machines which would be safe for the workman to handle and loved to invent devices which lightened domestic drudgery. Ferranti was a great engineer and lived to see his ideas developed and huge high pressure networks constructed in almost every country. Were it not for him the world would be perceptibly poorer to-day. He was a man of great modesty but much personal charm.

The premature death of Professor HUGH LONGBOURNE CALLENDAR has removed from our ranks an experimental physicist of great ability and insight. Elected Fellow of Trinity College, Cambridge, in 1886, he first devoted himself to the development of platinum thermometry as a means of very accurate measurement of differences of temperature. In 1893 he became Professor of Physics in McGill University, Montreal, and was largely responsible for the admirable equipment of the then new Macdonald Physics Laboratory. While in Montreal he began his researches on continuous

electrical calorimetry and had a wide influence in promoting interest in research in that University. After a short term of service in University College, London, in 1902, he was appointed Professor of Physics in the Imperial College of Science and Technology and filled this chair up to the time of his death. An unusually careful and accurate experimenter with marked interest in engineering applications, he devoted himself to accurate measurements of many important quantities in heat, and in this respect was a worthy successor of Regnault. One of his last pieces of work was the preparation and publication of accurate steam tables which have proved of great utility to industry. A man of wide training and all-round capacity, his death has left a gap in the scientific world which is difficult to fill.

EDWIN TULLEY NEWTON, who died in his ninetieth year, was for many years a leader in the study of fossils in Great Britain. Interested in natural history, he attracted the notice of Huxley and became his assistant. In 1882 he was appointed palæontologist to the Geological Survey and held this post until his retirement in 1905. Some of his most fundamental contributions to vertebrate palæontology are contained in three memoirs published in our "Transactions." He was elected to our Fellowship in 1893 and was awarded the Lyell Medal by the Geological Society.

MR. ALAN ARCHIBALD CAMPBELL SWINTON was a member of our Council at the time of his death. Trained as an electrical engineer he took an active part in the development of the electrical industry both as consulting engineer and as a director of many companies. A man of wide scientific interests he was one of the first to obtain X-ray photographs in this country, and was much interested and helpful in the early development of experiments on radio-communication. Of wide reading and sympathies, he was well known to scientific men and was a familiar figure in scientific gatherings. He was most interested in the work of the Society and served on a number of its committees as well as on the Council. The Society is much indebted to him for a generous gift of £1,000 in 1926 to form the nucleus of a General Purposes Fund.

KENNETH JOSEPH PREVITÉ ORTON passed away on March 16 last in his fifty-ninth year. After his student days at Cambridge, Heidelberg and London, he joined the chemical staff of the Medical School at St. Bartholomew's Hospital, and in 1903 became Professor of Chemistry in the University College of North Wales at Bangor. Orton carried out original work on the mechanism of organic chemical reactions and developed more particularly the study of the chlorination of aromatic compounds; he was one of the first systematically to apply

physico-chemical methods to the study of organic reactions. Orton was a vigorous and refreshing personality with many interests lying far outside his particular branch of chemistry; he was an experienced field geologist and ornithologist. He devoted himself with enthusiasm to the development of the University of Wales and his early death leaves all who are interested in Welsh education under a keen sense of loss.

JOHN OLIVER ARNOLD, who died on March 27 last, at the age of 71, was closely identified with the progress of the metallurgy of steel. Appointed while a young man to the Professorship of Metallurgy in the Sheffield Technical School, he saw the growth of that institution into the Applied Science Department of a University, and established a connection with the steel industry which has had lasting effects. It is largely due to his efforts that scientific control has been so generally adopted in metallurgical works, whilst his own researches did much to forward the application of metallographic methods, originally due to his fellow townsman, Sorby.

The death of JOSEPH ACHILLE LE BEL on August 6 last, takes from among us one of the veterans of French chemical science. In 1874, simultaneously with, but independently of, van't Hoff, Le Bel enunciated the doctrine of the asymmetric carbon atom and thereby laid the foundation of modern stereochemistry; it would be difficult to over-state the part which this fundamental theoretical conception has played in the development of structural organic chemistry. Le Bel, who was born in Alsace in 1847, received our Davy Medal in 1893, and was elected a Foreign Member of the Society in 1911. In 1925 he made a gift of money to the Society with the request "that you subsidise research rather than subsidise students, for I think we have plenty and to spare of savants who have fattened on examinations, but not enough of the people who employ their time in solving problems of interest. Hitherto the Royal Society seems to me to have used its money well. I hope that it will continue."

HERBERT HALL TURNER, who died suddenly at a meeting of the International Union of Geodesy and Geophysics, was Savilian Professor of Astronomy at Oxford. In 1893, when photography was beginning to be applied to the determination of positions of stars, he introduced the methods of reduction which have been employed with little modification ever since. He devoted himself very energetically to the project of the International Astrographic Catalogue, and having completed his own (Oxford) section in good time, rendered assistance to other observatories which were behindhand. He was also interested in variable stars and seismology, both of which subjects gave scope for his favourite

theme—harmonic analysis and the search for periodicities. He performed still greater service to astronomy by the infinite pains he took to assist and encourage the amateurs and the younger men and to keep in touch with those working in isolated observatories in the Dominions and elsewhere. A very ready speaker, a genial chairman and leader in any kind of activity, he will be greatly missed at astronomical meetings and conferences.

HAROLD BAILY DIXON entered Oxford with a classical scholarship in 1871, but soon turned his attention to science under the influence of Dr. A. Vernon Harcourt; in 1876 he commenced those experimental studies on gaseous explosion with which he was occupied until the morning of his death. During his early work he showed, contrary to the conclusions arrived at by Bunsen, that the explosion of gaseous mixtures is governed by Berthollet's "law of mass action"; he also discovered that carefully dried mixtures of carbonic oxide and oxygen cannot be ignited by an electric spark, and so opened up a new and fertile field of investigation which is still under exploration. Dixon carried out a large amount of difficult but very precise work on the high speed of travel of the explosive wave in gaseous mixtures and was the first to make careful measurements of the ignition temperature of such mixtures. In 1886 he was appointed to succeed Sir Henry Roscoe as Professor of Chemistry in Owens College, Manchester, a position which he held until 1922, when he was elected Honorary Professor in the University of Manchester. Although Dixon was intensely occupied throughout his life with scientific work of fundamental importance and far-reaching consequences, he devoted himself with enthusiasm to furthering the academic, social and athletic activities of his University. In this, his administrative gifts, his brilliance and felicity as an exponent, and his power of arousing enthusiasm in his students, made him again a commanding figure. As one of the foremost authorities on gaseous explosion, Dixon was frequently called upon to assist in Government enquiries into coal-mine disasters. He was elected to the Society in 1886 and was awarded a Royal Medal in 1913; he delivered the Bakerian lecture on "The Rate of Explosion in Gases" in 1893. On September 18 last he passed away suddenly in his seventy-ninth year, whilst retaining unimpaired until the end those mental gifts which so many of us have been privileged to admire.

WILLIAM DILLER MATTHEW, Professor of Palæontology in the University of California, was born in Canada, and though domiciled during the whole of his scientific career in the United States of America, retained the nationality of his birth. For thirty years he was associated with Dr. Henry Fairfield Osborn, in the charge of the great collection of fossil vertebrates in the American Museum

of Natural History, New York, to which collection Matthew's own discoveries in the Western States greatly contributed. In 1927 he accepted the chair in California, with the expectation of a long period yet before him for further work on the fossils of far Western America. His investigations and writings have played a large part in the development of knowledge of the extinct vertebrates and theories concerning their evolution, and the science of palæontology has suffered a heavy loss by his death at the early age of 59 years.

Dr. JOHN WILLIAM EVANS, who was admitted a Fellow of the Society in 1919, was a geologist of wide and varied experience. He had carried out important geological investigations in Southern and Western India, and in South America, besides occupying himself with many problems in theoretical geology. Of late years he had given much attention to the application of geographical methods to the study of the earth's crust.

I shall now pass to a discussion of some matters of general interest to the Society. In the Report of the Council for last year, it was announced that the Committee, which was appointed by the International Research Council to revise the statutes now in force, had adopted all the suggestions which the Council of the Royal Society had made. Since then the Committee's Report has been considered by the Executive Committee of the Research Council which has adopted it after making a few modifications and has recommended these revised statutes to the General Assembly for approval at its meeting in July, 1931. The changes introduced are all in the direction of giving to the Unions greater freedom in arranging their own affairs, the Council performing the function of a co-ordinating body. The Unions will be members of the International Council and will have representation in the General Assembly at its triennial meetings. The new Statutes are such as should facilitate that international co-operation in science which it is the aim of the organisation to promote.

At these anniversary meetings the President has frequently taken the opportunity of putting before the Society some recent and important development of science within the scope of his own personal interest. To-day, on this last occasion of my addressing the Society from this chair, I have felt rather disposed to look back over the whole term of my Presidency, and into that of my immediate predecessor, and to put on record some of my impressions of the work of the Society and of the way in which it is responding to the new opportunities for the promotion of science which have come to it in this present period.

I propose, then, to review briefly some aspects of the history of our Society since the end of the war, and to point out the way in which the responsibilities and work of the Society have increased during this period. While in the course of its long history, the Society has received numerous bequests for scientific and general purposes, shortly after the end of the war the funds at its disposal were greatly increased by the receipt of four major benefactions. I refer to the bequests of Miss Lucy A. Foulerton in 1919, of the late Dr. Rudolph Messel, F.R.S., in 1921, of the late Dr. Ludwig Mond, F.R.S., in 1923, and the notable benefaction of our valued friend Sir Alfred Yarrow, F.R.S., in 1923. Miss Foulerton's bequest was made specifically for the promotion of research in the Medical Sciences, while the terms of those by Dr. Messel and Dr. Mond and of the gift from Sir Alfred Yarrow allowed the Society a wider discretion to utilise the interest on the resulting funds for the general object of our Society, namely, the "improving of natural knowledge." Taking these benefactions as a whole, they provide resources for the promotion of research in practically the whole range of the natural sciences which our Society represents.

Under the Presidency of Sir Charles Sherrington, the Council considered with great care the best method of employing these new resources and decided to apply a large part of the incomes of the Foulerton and Yarrow funds in the first instance for the institution of Research Professorships. The first holder of such a Royal Society Professorship was the late Prof. E. H. Starling, appointed Foulerton Professor in 1922. A second Foulerton Professorship was created in 1926, Prof. A. V. Hill being appointed. On the death of Prof. Starling, a Foulerton Professorship was awarded to Dr. E. D. Adrian in 1929. In 1923, Prof. A. Fowler and Mr. G. I. Taylor and in 1924, Prof. O. W. Richardson were appointed Yarrow Professors of the Royal Society.

The Council further adopted regulations for the Messel and the Mond funds, subject to periodical review, which provided for the eventual use of these funds for the support of further professorships as the need and opportunity might arise. Wisely, as I think, they and their successors were content to watch for a time the general effect on scientific progress of the Foulerton and Yarrow appointments, holding meanwhile in reserve the similar opportunities which the Messel and Mond funds would enable them to offer. My close personal contact with him and his work enables me with special pleasure and warm approval to announce that this year the Council have appointed Dr. Peter Kapitza, F.R.S., Fellow of Trinity College, Cambridge, to a "Messel" Professorship of the Royal Society. I

shall have occasion later in my address to refer to the important researches on which Dr. Kapitza has been engaged in recent years, and to the arrangements made with the University of Cambridge for the provision and upkeep of a laboratory suitable for his investigations.

In my address to the Society in 1928 I reviewed briefly the work of the Royal Society Professors up to that date. As I then pointed out, we have been fortunate in securing the services of a group of men of marked research ability. There has been an output of work of high quality and importance, and I am sure we can all agree that this new experiment of endowing research professorships has proved an unqualified success. In all cases, the holders of our professorships have been heartily welcomed by the Universities and Institutions with which they were associated, and they continue to carry out their investigations under excellent conditions. I think there can be no doubt that the appointments so far made have not only added materially to the strength of the research side of the universities concerned, but have led to a marked increase of the research power of the nation.

While our Professors have been allowed a wide discretion in the work they perform, and in many cases direct the work of research schools, and give advanced courses of lectures, there is undoubtedly a general opinion that, at the present time, it would not be wise to increase unduly the number of our Research Professors. There is always the danger that any substantial increase in the number in the near future might lead, in a sense, to the segregation of some of the more vigorous elements in the research life of our Universities from that intimate contact with students and inspiration of their work which, in the case of many investigators of the highest rank, is an essential part of their contribution to the advancement of Science. In instituting these Professorships, the Society has been engaged in a novel experiment and, successful though the result has been, it is still desirable that we should proceed with caution and reconsider our policy from time to time as our growing experience suggests.

In addition to the six professorships which are supported from the trust funds obtained since the war, the Society now offers for the encouragement of younger research workers eight Studentships and Fellowships, namely, the Sorby, and Smithson Fellowships and the Foulerton, the Mackinnon, two Moseley, the Tyndall, and the Lawrence Studentships. The second Moseley Studentship has been established during the year in consequence of the augmentation of the Moseley fund by a bequest from the late Mrs. Sollas.

These Fellowships and Studentships are all financed from funds left to the Society for the specific purpose of their creation. In my address last year, I referred to the institution of a new Research Fellowship, financed from the bequest left by the late Mr. E. W. Smithson. The first appointment to this Fellowship has now been made and I shall say a few words later on the work of the new Fellow.

Taking into consideration the provision now made for the support of research, to mention only some of the major sources, by grants from the large Government funds administered by the Department of Scientific and Industrial Research and the Medical Research Council, by the studentships offered by the 1851 Commissioners, and by the Fellowships for research in the Medical Sciences created by the Beit Memorial Trustees, it is clear that financial support is now available from a number of different sources, for young research workers of promise in this country.

As I have pointed out, the funds held in trust by the Society for the furtherance of research in various branches of science have been very greatly increased during the past ten years and now amount to more than £600,000. The major increase occurred within the short period of five years from 1919 onwards, and the Council, fully conscious of its responsibility on behalf of the Society, in providing for the use of these great resources for the advancement of science, proceeded as I have indicated, with proper caution. After the appointment of the five first research professors, and the creation of the studentships for which certain bequests were specifically made, the Council had still a substantial margin of income from some of the larger funds, and this has been invested, while plans for its use to the best purpose were being matured. In this way about £72,000 has been added to capital, while in each year a considerable sum is still being received in dividends which has not yet been definitely allocated to any special research. Another reason for an initially cautious policy in expending these trust funds, was the difficulty of foreseeing the financial commitments of the Society due to its already existing activities. For example, the rapid increase of the volume of the Society's publication after the War, and the disproportionate rise in its cost, involved an increasing call on the funds available for this purpose. The Council at that time considered that one of the greatest services which they could render to Science, with the funds at their disposal, was to facilitate the publication of the results of research at a cost rendering them accessible to the widest range of scientific workers. The Council to-day have not moved from this opinion, but they have been able better to survey the Society's policy in relation to that of the scientific world in

general, and to estimate more clearly the probable needs of the future. It now seems unlikely that there will be any substantial increase in the amount of publication during the next few years. Moreover, the Council during the present year have given careful consideration to the cost of publication and have decided on an increase in the price of the Society's 'Proceedings' and 'Transactions' to external subscribers. Though the price is still low in comparison with that of other scientific publications and in relation to the increased cost of production, the change should result in the release of a substantial sum which can be allocated for other purposes.

It would, therefore, seem that the time has arrived when we may with prudence consider how some at any rate of the accumulated income from our trust funds may be best expended in promoting some form of scientific research.

Experience has shown that the encouragement of research by minor grants for special apparatus and material is in reasonable measure provided for by the Government Grant, supplemented from the Society's own research funds. The grants to individual investigators from such sources are usually small but suffice to assist materially important researches of a limited scope.

The situation, however, is very different when we consider large scale investigations of a pioneering character, which may require considerable financial support extending over a period of years in order to provide the necessary apparatus and technical assistance to bring the investigation to a definite conclusion. Few of our Universities or other Scientific Institutions are sufficiently well endowed to support large scale researches of this kind, even when the research appears of marked promise and when the idea and the man are forthcoming. In considering the best method of utilising the balance of the Society's present resources, the Council decided that it could best help the advance of science by assisting major researches of this character, and after careful consideration, were impressed with the fundamental importance of the researches at present being carried on by Dr. P. Kapitza, at Cambridge, and the need for continuing this work on a more permanent basis.

It may be helpful at this stage to give a brief history of the origin and development of the work on which Dr. Kapitza has been engaged for the past eight years. Trained as an electrical engineer, he was lecturer in Physics in the Petrograd Polytechnical Institute during 1918-1921. In 1921, he came to England and commenced research work in the Cavendish Laboratory, Cambridge. In 1922, he began experiments to test the possibility of

obtaining intense magnetic fields by sending very strong currents through a coil for such a short interval that the heating effect in the coil is restricted to a permissible value. With the assistance of a grant from the Department of Scientific and Industrial Research, special accumulators were constructed to give the necessary intense currents for a short interval of about $1/50$ of a second. In this way, fields up to 200,000 gauss were obtained, and it was found practicable to carry out experiments by this method, for example on the Zeeman effect and on the deflexion of α -particles. In order to carry these experiments still further, it was necessary to have a method of obtaining currents still larger and more under control. For this purpose, a generator of special design was constructed which gives, on short circuit, a current of about 70,000 amperes. The heavy current from the generator is passed for about one-hundredth of a second through a coil and is then broken by means of a specially designed automatic break. The Department of Scientific and Industrial Research gave a very substantial grant for the construction of this apparatus, while Sir William Pope kindly provided a temporary laboratory to instal the plant and to carry out the experiments. In 1926, the laboratory was opened formally by the late Lord Balfour, then Lord President of the Council, who had throughout taken an active interest in promoting these large scale experiments. This pioneering investigation, which was carried out in connection with the Cavendish Laboratory, was only made possible by the generous and bold support of the Department of Scientific and Industrial Research, which, up to the present, has defrayed the complete cost of the apparatus and of the subsequent investigations.

One of the chief difficulties in these experiments has been to construct a coil strong enough to withstand the enormous disrupting forces which arise when a large current is passed through the coil. A number of coils have been constructed which give magnetic fields of between 300,000 and 400,000 gauss over a volume of about 3 c.c. There appears to be no inherent difficulty why fields of the order of 1 million gauss should not be obtained, when called for, by this method. As the current through the coil only lasts for about $1/100$ second, oscillograph methods are used to determine the strength of the current and magnetic field and to follow the changes in the properties of the material under investigation. There is no special difficulty in conducting experiments with these momentary fields. In fact, a single photograph, obtained in $1/100$ of a second, may give a complete quantitative record of the magnetic effects produced in a material over a wide range of magnetic field.

The application of these new methods of producing intense magnetic fields

opens up a wide field of research where all magnetic properties can be examined in fields 10 to 30 times greater than those hitherto available by the use of electromagnets.

As soon as the apparatus was in working order, experiments were begun by Dr. Kapitza to investigate the change of resistance of crystals of bismuth in these intense magnetic fields from atmospheric temperature to that of liquid air. This was followed by an extensive investigation of the behaviour of a large number of metals under corresponding conditions. In general, it was found that the change of resistance was at first approximately proportional to the square of the magnetic field, but above a certain critical field, which varied from metal to metal, the change of resistance tended to become linear. On the basis of these new results, he has suggested a new way of looking at the phenomena which underlie the electrical conductivity of metals and its variation with temperature. Preliminary experiments have also been made on the action of these strong fields on the paramagnetism and diamagnetism of certain substances, while a new and sensitive apparatus has been constructed to study magnetostriction effects. An account of the apparatus and the experimental methods, together with the results of some of these investigations, has been published in our 'Proceedings.'

Magnetic phenomena are shown in their simplest form at very low temperatures when the complications due to the motion of the atoms and molecules are largely avoided. In order to obtain temperatures still lower than that of liquid air, a liquid hydrogen plant has been installed during the present year, and is now in working order. Preliminary arrangements have been made to instal a liquid helium plant when this is required for the investigations.

The grant given by the Department of Scientific and Industrial Research for carrying out these researches expires in a few years, while the laboratory temporarily lent for the purpose of these experiments is now required by the Chemical Department. The Department of Scientific and Industrial Research, by its broadminded and far-seeing action, has done a great service to science in thus supporting, through their initial stages, investigations having no obvious or immediate application in practice or industry. Their support for an indefinite further period, however, could hardly be part of the Department's policy. On the other hand, it appeared to the Society's Council, that investigations of this kind, in which new fields of knowledge are being opened up by new methods, had a peculiarly strong claim for support from those funds which they were holding ready for the furtherance of fundamental researches in pure science.

After full consideration, therefore, the Council, in addition to appointing Dr. Kapitza to a Messel Professorship, agreed to offer the University of Cambridge the sum of £15,000 for the building of a suitable laboratory within the next three years, provided the University was prepared to offer an appropriate site and to defray the running expenses of the new laboratory. Negotiations have taken place with the University of Cambridge and, though the matter has not been formally sanctioned by the University, the Council of the Society has received assurances which make them confident that the offer will be accepted and that the University will provide the necessary funds to carry out the work. If the University of Cambridge concurs with these proposals, the Royal Society will thus have been instrumental in founding a new and up-to-date laboratory, primarily designed for carrying out researches in intense magnetic fields, but at the same time providing the essentials of a modern Cryogenic Laboratory for the study of magnetic and other effects at the lowest attainable temperatures.

It is proposed that a Committee should be appointed, which would be responsible for the direction of the work of the Laboratory. The name of the laboratory has not yet been settled, but it would clearly be appropriate if it indicated the connection with the Royal Society and with the late Dr. Ludwig Mond whose bequest furnished the income from which the cost of the laboratory will be defrayed. It should be noted that among the purposes indicated in the will of Dr. Mond for the use of his bequest was "erecting new laboratories."

It will be remembered that, thirty years ago, this country was pre-eminent in the study of effects produced on matter by the low temperature produced with the aid of liquid hydrogen. It will be recalled that the late Sir James Dewar, with the technical assistance of Mr. Lennox, first produced liquid hydrogen in quantity in the Laboratories of the Royal Institution in 1898, and in 1899 the first solid hydrogen was obtained. It was as early as 1893 that Dewar devised the vacuum flask which has proved to be of such fundamental importance in the technique of low temperatures and has so greatly simplified the handling of liquid gases. It is of interest to note that it was decided in 1902 to construct a liquid hydrogen plant, of capacity of about 5 litres of liquid hydrogen per hour, as a British Government exhibit to the St. Louis Exposition in 1904. This plant was placed in the competent hands of Mr (now Sir) Joseph Petavel and I well remember the interest of his demonstrations of the properties of liquid hydrogen at that Exhibition. Some time later, a small liquid hydrogen plant was installed by Dr. Travers, of University

College, in the Laboratory of the late Sir William Ramsay. In the meantime, an efficient Cryogenic Laboratory had been established at Leyden, under the direction of the late Professor Kamerlingh Onnes, For.Mem.R.S. All of you are aware of his success in liquefying helium and of the wide range and importance of the investigations carried out on the effects of low temperatures on the properties of matter. It was only a few years ago that Prof. Keesom, who followed Onnes in the charge of this Laboratory, was successful in producing solid helium.

A few years ago, owing to the energy and enthusiasm of Professor J. C. McLennan, F.R.S., liquid hydrogen and helium plants were installed in the University of Toronto, and have proved their utility in a number of important researches. In recent years modern equipment for the liquefaction of hydrogen and helium has been installed in the Reichenhals, Berlin, by Dr. Meissner, and very valuable results have been already obtained. Dr. Franz Simon, of the University of Berlin, obtains the temperature of liquid helium by an ingenious method involving the use of liquid hydrogen and the absorption of helium gas by charcoal.

I am sure it will be gratifying to the Society to know that we may soon expect to have an up-to-date Cryogenic Laboratory on a small scale in this country, and thus to take part again in the exploration of this important field of enquiry.

I should emphasise the point that the Council in deciding to incur the liability of the expense of this new laboratory have utilised the income alone of certain trust funds, while the capital of each remains intact. There is still a substantial amount of income from these Trust Funds to be allotted, in accordance with the general aim adopted and kept in view by the Society's Council, for the furtherance of fundamental research in pure science. The policy which they may be expected to maintain in the future, is to keep watch over the whole field of scientific activity, in readiness to give help where there is promise of an important advance, and where the right man for its conduct is available. The Council look with confidence for help and support from the whole body of Fellows in the important responsibilities which they have accepted and have still to undertake on behalf of the Society.

I believe that it is in helping such important schemes of research that the Society can best utilise any research funds which it already possesses or which may become available in the near future. It not infrequently happens that a promising line of research or the development of a new method may be held up or abandoned because of the difficulty of obtaining adequate financial

support. In some important directions, advance can only be made with the help of technical assistance in the construction and use of special apparatus, in some cases on an almost engineering scale.

By its constitution, the Society is especially well fitted to advise and support investigations of this kind with a minimum of that bureaucratic control which is generally so distasteful to the original investigator. While with our modest funds, we can only hope to support a few of such undertakings, I am sure that if more funds were needed for such an important purpose they would soon be forthcoming. This extension of the activities of the Society, whereby it is taking an active and essential part in advising and assisting in the development of fundamental science in this country, cannot fail to have a vitalising effect not only on scientific workers in general, but on the Society itself. Along such general lines, it is not difficult to foresee that the Society will exert an ever increasing influence on the progress of science and thus promote still further the original intentions of its founders.

I referred earlier in my address to the institution by the Society of the *Smithson Research Fellowship*. The Society was fortunate in obtaining applications for this Fellowship from a number of distinguished investigators in different branches of Natural Science. The Selection Committee, consisting of representatives of our Society and of the University of Cambridge, did not find it an easy task to make a selection from among such an able group of investigators.

The first award of the *Smithson Fellowship* has been made to Dr. P. D. F. Murray. After a distinguished undergraduate career in the University of Sydney, Dr. Murray spent two years in research work in the Department of Comparative Anatomy at Oxford, and since 1926, has been lecturer in Zoology at the University of Sydney. Nearly all his work has been in the field of experimental embryology, and he has investigated with conspicuous success, the factors which determine the differentiation and shaping of the limbs and other parts of the body, mostly by the method of transplanting small portions of early embryos on to the chorio-allantoic membrane, where their development proceeds, apart from the influence of the other tissues of the embryo. By this procedure and by the method of tissue culture, Dr. Murray proposes to examine the cellular differentiation of the developing chick, which underlies the coarser morphology. He will work in the first instance at the *Strangeways Research Laboratory* in Cambridge.

Mr. A. H. White, for so many years in charge of the Library of the Society,

has retired this year on pension. Many of our Fellows and particularly our senior Fellows, are well aware of his devoted work in the interests of the Society for such a long period, and of his unrivalled knowledge of the Society's books and history. In recognition of these services, on his retirement, Mr. White has been given the title of Consulting Librarian to the Society. He has been succeeded in his office by Mr. R. Winckworth.

Before I pass on to the presentation of medals, my last official act before the termination of my Presidency, I should like to express my gratitude to the officers and Council of the Society for the consideration and kindness they have uniformly shown me. My path has been made easy by the very efficient help that I have received both from the present officers and those who have retired during my term of office. I would like also to express my thanks to Mr. Towle and the other members of the staff for their unvarying help and kindness. I can assure my distinguished successor from my own experience that he will find his work made pleasant by their ministrations. It has been a great honour for me to preside at your counsels and gatherings, and I can assure you that I have been happy to serve the Society to the best of my powers. I thank you all for this great opportunity and privilege of service.

The Copley Medal is awarded to Sir William Bragg.

To the rapid advance of Experimental Physics in the last thirty years, Sir William Bragg has made conspicuous contributions by his pioneering researches in Radioactivity, X-rays, and Crystallography. When Professor in the University of Adelaide, he was the first to realise, in 1904, the characteristic difference to be expected in the nature of the absorption of the massive α -particle and the light β -particles expelled from radioactive substances. His experimental researches brought out clearly the rectilinear path of the α -particles and their limited range of travel. In collaboration with his students, he examined in detail the variation of the ionisation of the α -particle along its path and its absorption by different kinds of matter. In his researches in X-rays and γ -rays, he was impressed by the difficulty that these high frequency radiations behaved like projected corpuscles—a difficulty which has only been in part resolved to-day. Following the discovery by Laue of the diffraction of X-rays by crystals, he was the first to develop a method for showing that ordinary X-radiation gave bright lines superimposed on a continuous spectrum. This reflection method of studying the spectrum of X-rays has proved of great importance to the development of knowledge. In the hands of Moseley, it supplied a means of showing that the

atoms have all a similar structure and that their properties are defined by a whole number. In the hands of Sir William Bragg and his son, Professor W. L. Bragg, it has provided a powerful tool for unravelling the structure of crystals. In this important development, which has added widely to our knowledge, Sir William Bragg has taken an active part, not only by his own researches, but by the direction of an important school of research on this subject at the Royal Institution. His work throughout is characterised not only by simplicity and elegance but by a clear grasp and exposition of the essential principles involved.

The Rumford Medal is awarded to Professor Peter Debye.

To Professor Debye are due many important advances in the field of heat and radiation. He introduced and developed a theory of the specific heats of solids which is of fundamental importance. By it, for the first time, the main phenomena relating to specific heats and their variation with temperature were quantitatively explained. He made important contributions to the theory of the scattering and reflection of X-rays. Independently of Compton, he put forward the quantum theory of the change of frequency due to the scattering of X-rays—the Compton effect. He was one of the inventors of the powdered crystal method of X-ray crystal analysis. By his introduction of the idea of spatial quantization and by his investigations relating to the electric and magnetic properties of molecules he did much to advance our understanding of radiation and molecular phenomena. In collaboration with Hückel, Debye has developed a theory to account for the properties of strong electrolytes which has many important applications.

A Royal Medal is awarded to Professor Owen Willans Richardson, F.R.S.

In his earlier work, Richardson had laid the foundation of Thermionics—a subject of the greatest theoretical and practical importance. He was the first to study in detail the escape of electrons from hot bodies in a vacuum and to give the correct interpretation of the phenomena. His investigations, continued over many years, led him to originate many of the fundamental ideas connected with the emission of electrons from hot bodies which are now universally accepted. His work on photo-electric emission was also of fundamental importance, and in it many of the now generally accepted ideas relating to interaction between radiation and matter were suggested. Among many important contributions in other fields was the prediction and calculation of the gyro-magnetic effect—the rotational torque accompany the

magnetisation of a rod. During the last ten years he has continued to make many important contributions towards the clearing up of difficulties in the subjects of his earlier investigations. In addition, he has done important work on electron emission associated with chemical action. He and his students have contributed largely towards filling up the gap between the ultra-violet and X-ray spectra. His main work in recent years has related to the hydrogen molecule, and has afforded a detailed test of the new quantum mechanics when applied to one of the simplest structures for which the old quantum mechanics breaks down. Richardson has throughout his work shown a most unusual combination of experimental skill and ingenuity with theoretical knowledge and insight.

A Royal Medal is awarded to Professor John Edward Marr, F.R.S.

At a time when few believed it possible Professor Marr discerned a delicate time-scale in the Lower Palæozoic Rocks, chiefly in the Lake District and North Wales, and applied it to elucidating the development of life and earth-structure. After testing his results in Scandinavia and in Bohemia he was able to make further use of them in setting in order corresponding rocks in South Wales. He has worked out the structure, origin and development of the mountains, lakes and rivers in Lakeland and elsewhere in the North of England, pioneer work which has been eagerly followed up by his pupils and successors. His work in association with Dr. Harker on the metamorphism brought about by the great mass of granite of Shap Fell on the rocks into which it was injected has become classic, and has inspired the rapid advance now being made in kindred studies. Of recent years he has contributed largely to knowledge of the Cambridge district, and particularly of the Pleistocene Deposits and their relation to Early Man there and in East Anglia generally. For some thirty years he gave invaluable assistance to Professor Hughes at Cambridge before succeeding him in the Chair. His labours during over forty-five years have been the chief instrument in establishing and maintaining the position in training and research now held by the Cambridge School of Geology.

The Davy Medal is awarded to Professor Robert Robinson, F.R.S.

By his investigations of the chemistry of the alkaloids, he has made notable additions to the knowledge of the structure of these complex substances, and by experiment extended by theoretical discussion he has strikingly indicated possible mechanisms of their formation in nature. His brilliant synthetical

work in connection with the colouring matters of flowers has greatly promoted the study of a group of substances of outstanding interest. His theoretical studies of the mechanism of organic reactions, in particular substitution in aromatic compounds, have led to results of great value in that they enable a very wide range of reactions to be considered from a common point of view.

The Darwin Medal is awarded to Professor Johannes Schmidt.

The Darwin Medal is given in reward of work of acknowledged distinction in the field in which Charles Darwin himself laboured. When it is remembered that the store of knowledge which Darwin accumulated on board the "Beagle" in her voyage round the world was the foundation of all his later thought and of his outlook on biological problems, the conditions of the award are without doubt fulfilled in the person of Dr. Johannes Schmidt, at the same time a distinguished oceanographer, and a recognised research worker in genetics of animals and plants. The number and extent of the voyages in small research vessels which Dr. Schmidt has accomplished with success, his large and varied collections of the pelagic fauna and flora, and the remarkable series of observations, made under his direction, on the physical and chemical phenomena of the sea, give him an undisputed place in the first rank of those scientific explorers whose labours have built up our knowledge of the oceans of the world. His researches on the life-history of the freshwater eel and the discovery of its breeding places far out in the Atlantic have proved of such general interest that they are almost as well known and appreciated by the general public as they are accepted and valued by his fellow-biologists, although in reality these researches constitute a comparatively small part of his real contributions to the science of the sea. It has already been said that, in addition to his work of marine exploration, Dr. Schmidt has devoted great attention to the fundamental problems of the science of genetics. His breeding experiments on the tropical freshwater fish, *Lebistes*, carried out in the Carlsberg Physiological Laboratory at Copenhagen, of which he is a director, are of much interest, whilst his investigations on the local races of the viviparous blenny (*Zoarces viviparus* L.) are of outstanding importance and originality.

The Hughes Medal is awarded to Sir Venkata Raman, F.R.S.

Sir Venkata Raman is one of the leading authorities on optics, in particular on the phenomenon of the scattering of light. In this connection, about three years ago he discovered that the light's colour could be changed by scattering.

This had been predicted theoretically some time before, but in spite of search the change had not been found. The "Raman Effect" must rank among the best three or four discoveries in experimental physics of the last decade. It has proved, and will prove, an instrument of great power in the study of the theory of solids. In addition to important contributions in many fields of knowledge, he has developed an active school of research in Physical Science in the University of Calcutta.

On the Surface Potentials of Unimolecular Films of Long Chain Fatty Acids.—Part I. Experimental Method.

By J. H. SCHULMAN and ERIC K. RIDEAL, F.R.S., Laboratory of Physical Chemistry, Cambridge.

(Received June 12, 1930.)

Introduction.

Molecular orientation in a film formed at an air liquid interface was ascribed by Hardy* to an inwardly directive attractive force along the normal to the surface, the condition of minimum potential involving two terms, one relating to the variation in density, the other to the orientation of the field of force. A great impetus was given to the study of films by Langmuir† who identified in a complex molecule those portions having large stray fields with the "polar" groups, which are accordingly attracted inwards towards the bulk phase. That "polar" groups do in fact possess large fields is confirmed from an examination of the electric moments of compounds containing these groups. In previous communications‡ it was shown that the characteristics and phase of films could be affected not only by alterations in the variables of temperature and two dimensional pressure as shown experimentally by Langmuir and by Adam, but also by altering the extent of the adhesion of the asymmetrically situated polar group to the substrate. Alterations in the extent of this adhesion will naturally affect the field and it is the object of this communica-

* 'Proc. Roy. Soc.,' A, vol. 88, p. 303 (1913).

† 'J. Amer. Chem. Soc.,' vol. 39, p. 1848 (1917).

‡ Lyons and Rideal, 'Proc. Roy. Soc.,' A, vol. 124, p. 323 (1929).

tion to attempt an examination of the behaviour of films from this point of view.

The modification of an interfacial potential difference produced by the presence of a unimolecular film was shown by Helmholtz to be given by the expression

$$4\pi n\mu = \Delta V$$

where the change in potential ΔV is caused by n molecules per square centimetre of the film forming substance, each molecule possessing an average electric moment of effective vertical component μ .

The validity of this expression is dependent on the constancy of the value of μ both with the temperature and with the state and closeness of packing of the molecules in the film. In respect to the effect of closeness of packing on the value of μ both the experimental data of Becker* on the thermionic properties of unimolecular films of the alkali metals, and the variation of the dielectric constants with the temperature of substances showing the property of association (Debye, 'Polar Molecules') lead us to anticipate that the effects of mutual induction between the molecules in such films may not be negligible.

The influence of temperature on the value of μ for long chain fatty acids when occupying a definite area on the surface of water is likely on account of their size and orientation to be small. In the case of a simple dipole of moment μ inclined at an angle θ to the normal we obtain

$$\Delta V = 4\pi n\mu \cos \theta,$$

and if this angle is governed only by the electric forces and thermal agitation $\cos \theta$ may be replaced, as shown by Debye ('Handbuch der Radiologie,' p. 617) by the Langevin function $L(x)$ where x is $2\pi n\mu l/K \cdot T$. In the case of long chain acids floating on the surface of water the effective electric moment is made up of a number of component parts, including the difference in moment caused by replacement of the water surface by the terminal carboxyl groups and the compensating ionic double and diffuse layer under the sheet of polar head groups brought into existence by the presence of the polar sheet. That such double and diffuse layers exist under films can be concluded both from the experiments of Alty† on the cataphoresis of air bubbles, and of McBain and Peaker‡ on the conductivity of liquid in contact with surface films. Also,

* 'Phys. Rev.,' vol. 33, p. 1082 (1929).

† 'Proc. Roy. Soc.,' A, vol. 106, p. 316 (1924), vol. 112, p. 235 (1926), and vol. 122, p. 633 (1929).

‡ 'Proc. Roy. Soc.,' A, vol. 125, p. 344 (1929).

as we shall note, they are essential to the stability of films during the critical region of a change of state.

Thus the effective electric moment and the measurable vertical component is the result of the algebraic summation of a number of separate terms, not readily evaluated individually. Any enquiry into the influence of temperature on the value of μ should clearly be restricted in the first instance to the simplest possible systems. The first systematic investigations of an air water interfacial potential difference was made by Kenrick* who noted large changes of potential on the addition of capillary active materials to a dilute solution of potassium chloride. His method of measurement, which in an improved form has been employed by Frumkin,† consisted in measuring the potential difference between a jet of solution flowing down the axis of a vertical tube and a stream flowing down the internal sides of the tube. These investigations were extended by Guyot and by Frumkin.‡

Guyot's method differed from that of Kenrick in that he ionised the air gap between a metal plate and the surface of the solution by means of a radioactive salt. Since only differences of potential are measured the potential difference across the interface due to the charge caused by ionisation could be neglected.

Guyot showed by placing an increasing number of drops of a weak benzene solution of fatty acid on the surface that the surface potential was directly proportional to the concentration over certain ranges which we now term the expanded state; and attributed the constancy of μ to a limiting orientation of the molecule. The expansion of Labrouste§ was clearly observed. Owing to his method of working Guyot failed to notice the transitions between the vapour and expanded and the expanded and solid condensed states respectively, obtaining only metastable expanded films and part of the stable expanded state. Over this region, as will be shown, the molecular electric moment is constant, and is one in which Guyot obtained a direct proportionality between the increase in surface potential and the surface concentration.

He obtained a value of $\mu = 2.09 \cdot 10^{-19}$ e.s.u. for myristic acid in this state, but his calculations are marred by an arithmetical error, in that the Avogadro number was taken as $6.7 \cdot 10^{23}$ instead of $6.06 \cdot 10^{23}$. With this correction a value of $\mu = 2.30 \cdot 10^{-19}$ e.s.u. is obtained in close agreement with the value

* 'Z. Phys. Chem.,' vol. 19, p. 625 (1896).

† 'Z. Phys. Chem.,' vol. 109, p. 34 (1924).

‡ Guyot, 'C. R.,' vol. 159, p. 307 (1914) and 'Ann. Physique,' vol. 10, p. 508 (1924); Frumkin, 'Z. Phys. Chem.,' vol. 111, p. 190 (1929) and vol. 115, pp. 190, 485 (1925).

§ 'Ann. Physique,' vol. 14, p. 164 (1920).

obtained in this work. Guyot was unaware of the existence of either the liquid condensed or solid condensed states and ascribed the differences in value between palmitic acid $\mu = 2.65 \cdot 10^{-19}$ e.s.u. and myristic acid $\mu = 2.3 \cdot 10^{-19}$ e.s.u. to experimental error. Guyot and Frumkin concluded that the limiting potential difference obtained when an excess of the material was placed on the surface was characteristic for the substance, and also from somewhat inadequate experimental data, that the surface potential was independent of the underlying solution except for effects due to ionisation or solution of the film-forming substance. In previous communications (*loc. cit.*) the variation in the crystal equilibrium spreading pressures of films with the nature of the substrate has been demonstrated, and as will be noted similar variations in the values of the surface potential are obtained. Frumkin's extensive investigations reveal great changes in effective moment with the constitution of the polar head, and he has obtained numerous values for ΔV_{∞} , the limiting potential differences with excess of the film-forming material. Since the numbers of molecules per square centimetre of surface for different substances are not identical when the characteristic values of ΔV_{∞} on a particular substrate are attained, the interpretation of these values in terms of the chemical constitution of the polar head group cannot be regarded as more than semi-quantitative in character. Although he and Williams* conclude that the value of μ does not change with the surface concentration yet from experiments with capillary active soluble materials many of his values for the ratio of $\Gamma/\Delta V$ where Γ is the surface excess calculated with the aid of von Szyzskowski's equation show marked variations. Whilst no definite conclusions can be drawn from his data, not only on account of the insufficient accuracy of the experimental method for the evaluation of small values of ΔV , but also on account of the probable inexactitude of von Szyzskowski's equation, in which concentrations instead of thermodynamic concentrations are used, yet the inference that μ is actually independent of Γ , the surface concentration, under all conditions is certainly not definitely confirmed by experimental proof.

It has been found possible to develop the method of surface potentials so as to give us information new and distinct from that given by the trough method on the molecular architecture of unimolecular films. This method also permits us to study, although in less detail, the distribution of ions in the substrate below the films, and also to follow the process of chemical reactions

* 'Proc. Nat. Acad. Sci.,' vol. 15, p. 400 (1929).

taking place in the film material. It is hoped with increasing experience in technique to develop this latter phase of the investigation in some detail.

In the following pages an attempt is made to study the change in surface potential, and thus the effective vertical component of the molecular electric moment, for fatty acid films in the vaporous, liquid (or expanded), the meso-phasic (smectic or liquid condensed state), and the solid condensed states respectively, as well as the effect of variation in the two dimensional pressure F on the values of μ .

Experimental Method.

The method employed for the experimental examination was essentially that of Guyot and of Frumkin, but suitably modified to attain an accuracy in measurement of the potential differences of at least ± 2 millivolts. The

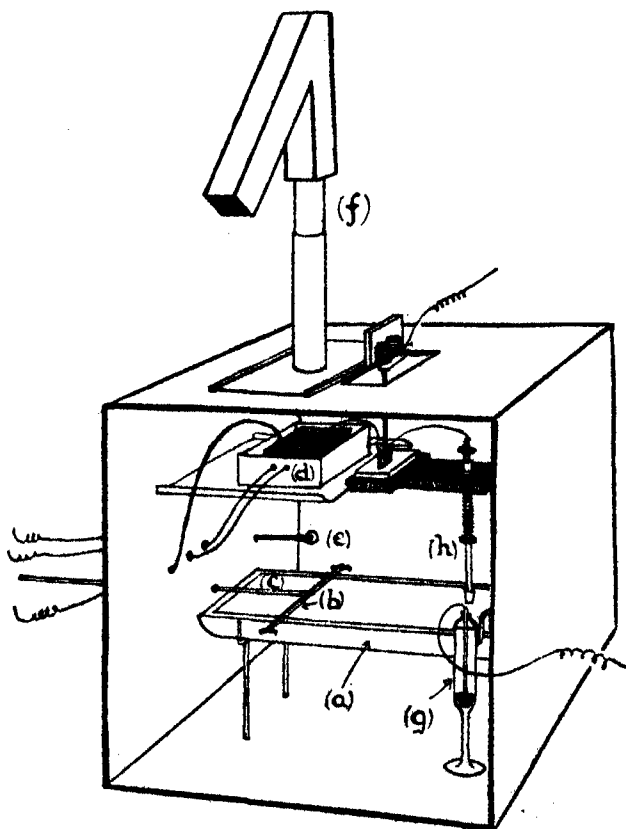


FIG. 1.

apparatus consisted of a small glass trough with bevelled edges (*a*) 23 cm. $\times$ 10.5 $\times$ 2 cm. dimensions. To constrict the area of film placed upon a water surface in the trough a glass slide (*b*) operated by a horizontal glass rod with prongs (*c*) was employed. Both slide and trough edges were repainted after each experiment with a benzene solution of recrystallised paraffin wax, an operation found indispensable when small surface concentrations of capillary active materials were being examined. The trough was inserted in a well-earthed Faraday cage provided with a wire gauze celluloid covered window for inspection, and with a small aperture for the glass rod (*c*) which operated the slide constricting the trough area. Inside the cage was placed on a support a Lindemann electrometer (*d*) of sensitivity of 4 millivolts per division, the electrometer being employed as a null instrument; the shadow of the needle cast with the aid of a small lamp (*e*) being observed through a periscope (*f*) on an etched glass scale. One electrode consisted of a calomel electrode (*g*) making contact with the liquid in the trough, and, to eliminate liquid-liquid junction potentials, the same solution was employed to make up the calomel electrode as was used in the trough. In preliminary experiments the air electrode (*h*) consisted of a platinum plate of 1 cm. area, this being eventually replaced by a brass disc and holder to which a piece of platinum wire 0.5 mm. in diameter and 5 mm. long was attached.

One milligram of radium bromide was dissolved in 10 per cent. nitric acid to which 5 mgm. of lead nitrate was added and the polonium in the solution was deposited electrolytically on the platinum. We are indebted to Sir Robert Robertson for the radium and to the Cavendish Laboratory for a further supply of polonium with which to extend the investigations. The adequate insulation of the connection between the air electrode and the electrometer needle proved to be the greatest technical difficulty to be overcome. After a number of experiments the following method proved satisfactory. The brass disc holding the polonium coated wire was connected by means of a copper rod to an adjustable spring regulated by a screw so as to adjust the height of the tip of the wire above the surface of the liquid in the trough. This spring and screw were placed in a small ebonite block which was moulded with sulphur into an ebonite tray, forming a miniature drawbridge by means of a hinge attached to a large piece of ebonite supporting a sulphur block. By means of a thin silk string passing through the top of the Faraday cage the drawbridge could be raised or lowered so as to bring the air electrode into position over the water surface. Wires from the air electrode and the Lindemann electrometer needle were brought to two small mercury cups formed in a block of

solid paraffin on the sulphur block and by means of a small electromagnet operating a copper bridge piece (which can be earthed) connection from the electrometer needle either to the air electrode or to earth could be established from the outside of the Faraday cage. The usual connections are made to the Wheatstone bridge as well as the potential system for regulation of the plate voltage of the electrometer. Frequent baking of the ebonite and scraping of the sulphur were found to be necessary operations to ensure consistency of the potential difference measurements. To obtain accurate determinations over the sensitive ranges, *i.e.*, for vaporous films, the experiments were carried out on a brickwork platform built up in a cellar maintained at a uniform temperature. Buffer solutions were made up according to the directions of Clark ("The Determination of Hydrogen Ions") with freshly distilled grease-free water. The palmitic acid (Kahlbaum) was recrystallised three times from alcohol, the myristic acid was kindly provided by Dr. N. K. Adam and the pentadecylic acid by Prof. W. Garner. Stock solutions were prepared in freshly redistilled (62°–63°) petrol ether solution, since it was found that higher boiling point distillates as well as benzene remained for long periods of time entangled with the film on the surface causing fluctuations in the interface potential. A calibrated dropping pipette was employed and the solutions and pipette deliveries were checked by measurement of force area curves on a Langmuir trough apparatus of the type constructed by Adam and Jessop.* The measurements were found to agree to within 2 per cent. of the values cited both by these workers and by Lyons and Rideal (*loc. cit.*). After cleaning the surface with slides until a steady potential was reached the polonium coated wire being placed in position about 5 mm. above the surface by means of the drawbridge after every cleaning operation, a film was spread on the surface, the drawbridge lowered and the alteration in the potential difference caused by the film then determined.

On testing the zero potentials for experiments of long duration, it was found that variations of only 1 to 2 millivolts were experienced for periods of 4–6 hours. For this purpose the trough was hermetically sealed into the Faraday cage to avoid all dust and special precautions were taken with the insulation of the lead from the polonium-coated wire to the needle of the electrometer. Both the trough and electrometer were operated entirely from outside the Faraday cage.

* "Proc. Roy. Soc., A, vol. 110, p. 423 (1926)."

The Behaviour of Myristic Acid.

Two methods were employed for spreading films of this acid on the surface of N/100 HCl. The first, that of surface solution of a crystal* by which films could be obtained without the aid of any mechanical contrivance. This usually resulted over the sensitive regions, such as the vaporous state and all phase transitions, in giving slight distortional or hysteresis effects in the films; by this method only rough estimations of the molecular areas could be obtained. The second method, that of spreading the materials with the aid of petrol ether solutions and compressing the films by means of slides gave the exact area measurements on the phenomena observed in the former procedure.

On placing a small crystal of myristic acid on the surface of water, surface spreading occurs (*loc. cit.*) and the surface tension of the water falls until the two dimensional pressure effecting the transition, vapour to liquid (expanded) film is reached. Surface solution with increase in the area of liquid or expanded film at the expense of the area covered with a vaporous film then proceeds at constant pressure. When the whole surface is covered with an expanded film the value of F then rises rapidly, and finally attains a new constant value when the crystal equilibrium film pressure is reached. On the F time curve there is thus a period of arrest corresponding to the transition vapour to expanded liquid film and a final value of F characteristic of the material spreading, the composition of the substrate and the temperature.

A stiff platinum wire coated with myristic acid possessing a circumference of 0.4 cm. was held by an insulated stand vertically in the surface of N/100 HCl solution in the trough. The rate of rise of the value of ΔV thus obtained is shown in fig. 2 (*b*). The curves (*a*) and (*c*) were obtained with other acid-coated wires. It will be observed that an arrest is obtained at 150 to 160 millivolts, the value being dependent on the temperature, for a period of some 10 minutes with the larger crystals and of 20 minutes with the smaller crystals.

We thus obtain the interesting result that over this period of arrest fresh molecules are entering the film, but there is no corresponding change in ΔV ; the mean value of μ must thus be sinking. We can make an approximate calculation of the molecular areas at the beginning and end of the arrest period. The rate of surface solution from a crystal of myristic acid is $4.5 \cdot 10^{18}$ molecules per second per centimetre of line in contact with the water at 16° C. With a trough area of 210 cm.² and an interfacial line of 0.4 cm. we obtain as mean molecular areas in the film at the commencement and end of the region

* Cf. Cary and Rideal, 'Proc. Roy. Soc.,' A, vol. 109, p. 318 (1928); Adam and Jessop, *ibid.*, vol. 110, p. 441 (1929).

of constant potential of $97 \text{ \AA}^2$ and $52 \text{ \AA}^2$ respectively. In confirmation of these values, measurements employing the dropping pipette and the standard solution of myristic acid gave values of $88\text{--}92 \text{ \AA}^2$ and $53.5 \text{ \AA}^2$ as the commencement and end of this region.

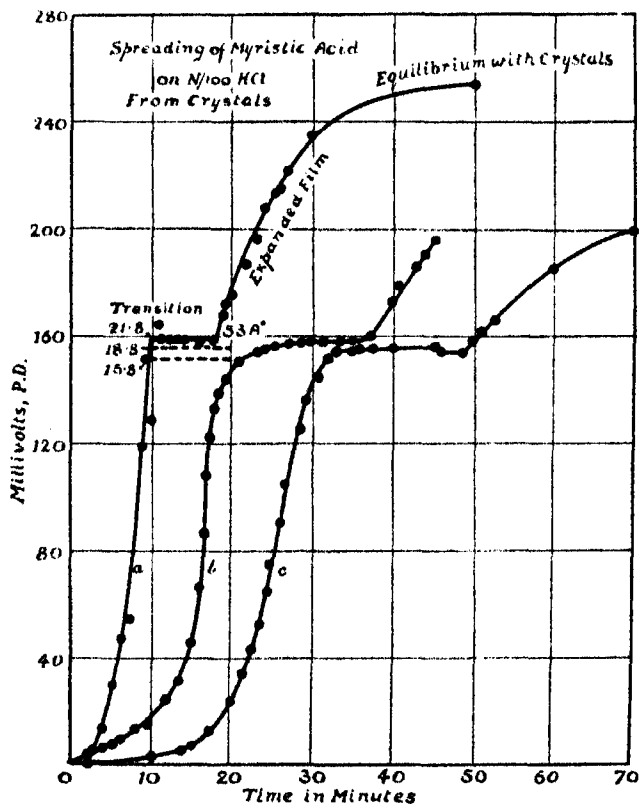


FIG. 2.

In figs. 3 and 4 are plotted the values of ΔV obtained against the mean molecular area in a film obtained by spreading from petrol ether, the film being compressed in the usual way so as to obtain areas which are smaller than that corresponding to the crystal equilibrium pressure.

Great care had to be exercised in obtaining reproducible values for ΔV for areas greater than $100 \text{ \AA}^2$. In dropping the petrol ether on to the water surface it was noted that after evaporation of the ether the potential did not acquire a constant value for some time. This fluctuation appears to be due to rapid evaporation of the ether leaving small portions of the film not in the vaporous but in a condensed state, these patches undergoing subsequent surface solution to attain the equilibrium conditions imposed by the temperature and area of

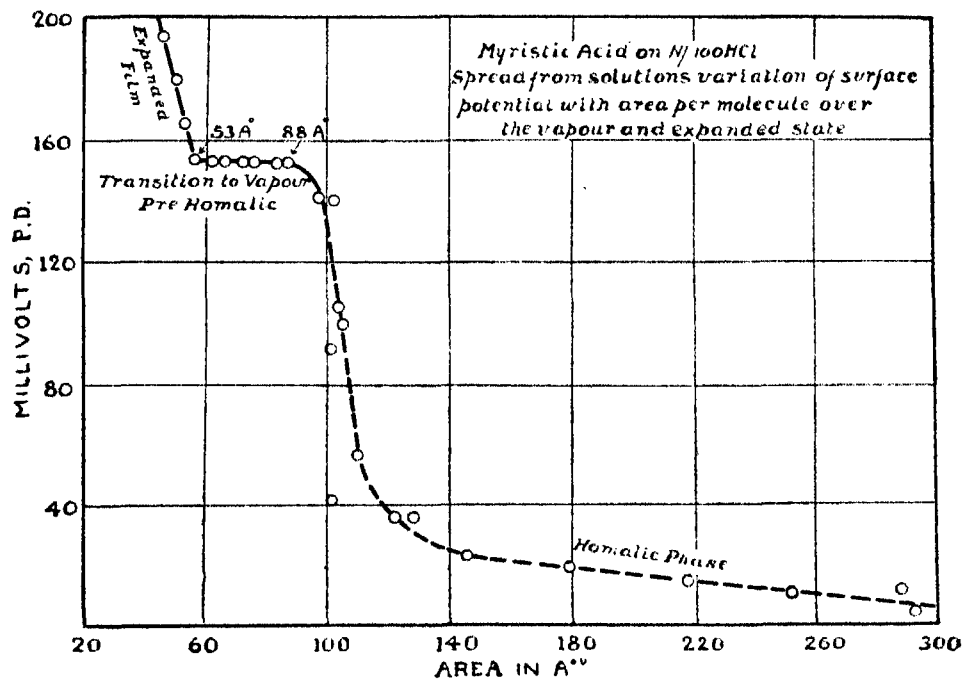


FIG. 3.

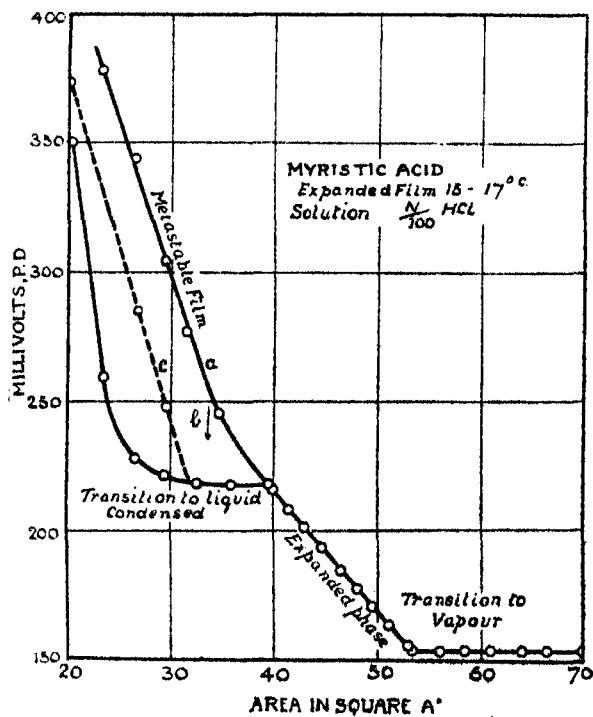


FIG. 4.

the water surface available. The fluctuation was found to be particularly pronounced in the case of palmitic acid where the rate of surface solution at these temperatures is extremely slow.

Whilst with due precautions the values given in the curve could be obtained repeatedly both on expansion and on contraction of a film, there were found to exist two critical regions in which effects due to hysteresis were most marked. One was noted over the region of area 88 to 100 Å². By careful expansion of the film from 88 Å² areas as large as 105 Å² could occasionally be obtained before any change in the potential occurred. Even more marked were the effects due to hysteresis over the region of areas 40 Å² to 30 Å². On rapid compression of the film to areas below 40·0 Å² and potentials above 218 mv. the "metastable" curve (fig. 4 (a)) could be obtained, quite reproducible in form. The values for ΔV remain constant for a minute or so and then fall (e.g., along (b), fig. 4) attaining the constant value of 219 mv. over the whole range of compression 40 Å² to 30 Å². Whilst the attainment of the equilibrium value of 219 mv. was relatively rapid from areas of 35 Å² and less for areas between 35 Å² and 40 Å² it was slow, but by waiting for as long as 5 minutes the limit of area for constant equilibrium potential was fixed definitely at between 39 and 40 Å².

If at any point during the compression over the range 40 Å to 30 Å² the rate of compression was suddenly augmented metastable potentials of high value could be obtained; an example of such is shown in fig. 4 (c).

The Expanded, Liquid Condensed and Metastable States.

From the figs. 3 and 4 it will be noted that in the ΔV area curves for myristic acid there exist three well defined arrest points, viz., 39·5, 53·5 and 88 Å², with a less well defined one between 26 and 30 Å².

N. K. Adam ("The Physics and Chemistry of Surfaces," Oxford Press) finds that the transition between the expanded or liquid film and the condensed liquid film commences at 35 Å² at 16·3° C. There seems little doubt that this transition of condensed to expanded film as measured by the method of surface potentials commences at 39·5 Å².

The commencement of the transition of the expanded state into the vapour state is quite clearly marked at 53·5 Å²; whilst Adam states (*loc. cit.*, p. 68) "the area of the expanded curves extrapolated to zero compression is about 48 Å², the limiting area is in fact difficult to measure with exactitude by the trough method at the low pressure of 0·20 dynes per centimetre where the transition takes place.

The region of the expanded film by the method of surface potentials accordingly extends from 39.5 – $53.5 \text{ \AA}^2$, and over this region the interfacial potential difference increases proportionally to the number of molecules in the film.

It is important to notice that the interfacial potential difference also increases proportionally to the number of molecules in the film over the metastable expanded phase from 39.5 – $25 \text{ \AA}^2$; if a film is placed on the surface with a molecular mean area of between 40 – $25 \text{ \AA}^2$ by means of drops from a petrol ether solution, the film is nearly always in this metastable expanded state and the values are therefore constant; it was in this region that most of the experimental work of Guyot and of Frumkin was carried out.

On the Surface Potentials of Unimolecular Films of Long Chain Fatty Acids. Part II.—The Evaluation of the Resolved Electric Moments.

By J. H. SCHULMAN and ERIC K. RIDEAL, F.R.S., Laboratory of Physical Chemistry, Cambridge.

(Received June 12, 1930.)

In Part I a method was described for the determination of the change in interphase potential at an air liquid interface caused by the presence of a unimolecular film of myristic acid and the values for this change (ΔV) were plotted as a function of the molecular area.

On application of the Helmholtz equation

$$\Delta V = 4\pi n\mu$$

we obtain a mean value for the vertical component of the molecular electric moment of a molecule of myristic acid when present in a film in the expanded state of

$$\mu = 2.29 \cdot 10^{-19} \text{ e.s.u.}$$

A value for μ can also be obtained from the slope of the $\Delta V_1 n$ curve which on extrapolation to the value of $n = 0$ evidently does not pass through the origin where $\Delta V = 0$, i.e., by considering the variation in surface potential due to a change in the number of molecules per square centimetre by comparing the values of the potentials over the range 53.5 – $40 \text{ \AA}^2$ then

$$\bar{\mu} (\Delta V_{40} - \Delta V_{50}/4\pi (n_{40} - n_{50}) = 2.50 \cdot 10^{-19} \text{ e.s.u.}$$

There is thus a mean difference of $2.50 - 2.29 = 0.21 \cdot 10^{-19}$ e.s.u. in the values of the moment obtained by the two methods.

This difference must be due to a change in the zero potential after the deposition of an expanded film on the surface, so that on the subsequent addition of molecules the increment in potential must be taken with the new zero potential.

The zero potential at the air liquid boundary is due partly to an adsorbed double layer of hydrogen and chlorine ions (*cf.* Frumkin, *loc. cit.*). A repulsion of chlorine ions and an attraction of hydrogen ions at the surface due to the presence of the film would cause the zero potential to become more positive and so cause a change in the true value of $\bar{\mu} = 2.50 \cdot 10^{-19}$ e.s.u. to the apparent value of $2.29 \cdot 10^{-19}$ e.s.u.

A study of the potential changes due to the adsorbed ionic double layers and their influence on the surface potential of thin films will be given in Part III.

In the transition from the expanded to the liquid condensed states (fig. 4, Part I) the value of ΔV remains nearly constant. If we imagine the film compressed to such an extent that the mean molecular area is some $33 \text{ \AA}^2$, then half the film must be in the liquid condensed or smectic state and half the film in the expanded or liquid state. Since these phases are in equilibrium with one another the work done in taking an electron across the interface in either state must be the same, but the ratio of the number of molecules of the film in each state is not unity but in the ratio condensed : expanded approximately 40 : 25 or 8 : 5, thus the values of the moments of myristic acid in each state must be in the ratio 5 : 8 giving a mean value for $\bar{\mu}$ in the liquid condensed state of $\frac{5}{8} \times 2.5 \cdot 10^{-19} = 1.56 \cdot 10^{-19}$ e.s.u., a value in agreement with that attained by extrapolation to $A = 25 \text{ \AA}^2$ from the curve in fig. 1, where μ the vertical component of the electric moment is plotted against the molecular area, the former being derived from the surface potentials with the aid of the Helmholtz equation.

The values of $\bar{\mu}$ on N/100 HCl are accordingly $1.56 \cdot 10^{-19}$ e.s.u. for a molecule in the liquid condensed state at the pressure corresponding to equilibrium with the expanded state and $2.5 \cdot 10^{-19}$ e.s.u. for a molecule in the film in the expanded state, this value being independent of the molecular area.

From fig. 4, Part I, it will be seen that the effect of pressure on the film in the condensed state is to cause a rapid rise in the surface potential and thus in the electric moment. This effect of pressure on the films in the condensed state is more readily examined in the case of palmitic acid which will be discussed later. The electric moment of the molecule in coherent films is

thus smallest and constant in the smectic or liquid condensed state and rises on conversion into both the expanded and into the solid condensed state.

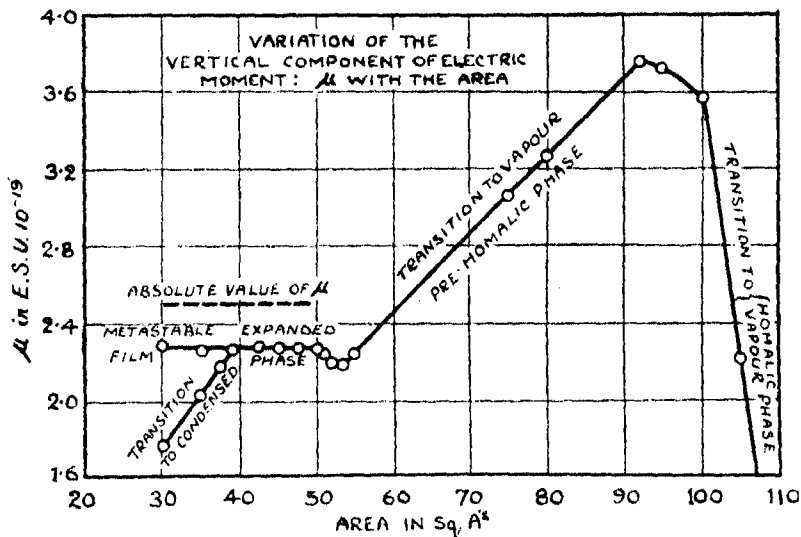


FIG. 1.

The mesophase therefore represents the most stable arrangement for the molecular architecture which is in agreement with the freely tilted molecule structure proposed by Lyons and Rideal (*loc. cit.*).

A further examination of the behaviour of $\bar{\mu}$ with the area of the molecule in fig. 1 indicates that the vertical component of the electric moment in the metastable state resulting from rapid compression of an expanded film is the same as the component $\bar{\mu}$ for a molecule in the expanded state, viz., $2.5 \cdot 10^{-19}$ e.s.u., but that if time be given, the metastable state will change into the more stable orientated liquid condensed state with the corresponding value of $\bar{\mu} = 1.56 \cdot 10^{-19}$ e.s.u. Likewise the variation of the component $\bar{\mu}$ in the two transition states between the expanded film and the liquid condensed and the expanded and the vapour states respectively, where the molecules are in all probability in a horizontal position, clearly illustrates the de-orientation or tilting effects which must take place in a molecule in its transition from the condensed to the vapour states (*cf.* Lyons and Rideal (*loc. cit.*)), i.e., that the state of the film is dependent on the tilt of the molecule.

The Vaporous and Transition State.

From the curves (figs. 3 and 4, Part I) it will be noted that the transition from the expanded or liquid state (53.5 Å^2) to the vaporous state (90 Å^2)

occurs at constant potential, therefore the mean resolved electric moment must be steadily increasing to a maximum. As can be seen (fig. 1) this maximum value of $\mu = 3.73 \cdot 10^{-19}$ e.s.u. is reached at $92 \text{ \AA}^2$ where a very remarkable change takes place in the surface potential, and thus in the molecular electric moment. When the area exceeds $100 \text{ \AA}^2$ there is a rapid fall both in the potential and in the value of μ , this fall being almost complete at $120 \text{ \AA}^2$ (fig. 3, Part I). It seems difficult to avoid the conclusion that there must be an intermediary state between the expanded and vaporous states. That such a transition must exist is rendered likely on consideration of the process of two dimensional vaporisation and condensation going on between the liquid and vaporous states. Whilst it is easy to visualise the process of two dimensional vaporisation, as the tearing away of an inclined molecule from the edge of the liquid phase, and the detached molecule then falling down on the surface to assume a horizontal position as exists in the vaporous state, it is not easy to picture the mechanism of the reverse process. If, however, extension of the liquid or expanded phase can proceed to $100 \text{ \AA}^2$ when the area of water surface available per molecule is just sufficient to permit of the molecule acquiring the horizontal position which it normally preserves in the vaporous state, the sudden fall of the electric moment at $100 \text{ \AA}^2$ is readily accounted for*, and the mechanism of two dimensional vaporisation and condensation from a horizontally inclined liquid phase rendered intelligible. The expansion of the liquid or expanded phase from $53 \text{ \AA}^2$ to $100 \text{ \AA}^2$ takes place according to measurements on the Langmuir trough at a constant pressure equal to the vapour pressure of the liquid phase. We notice that the electric moment per molecule is increasing over this region of expansion, due either to diminishing association of the molecules, or, what is more probable, to a change in the direction of the vector of the electric moment as the molecules change their orientation. It is convenient to term these intermediary states between the normal liquid and the normal vaporous state as the pre-homalic and homalic states respectively. See fig. 1 (and fig. 3, Part I).

The fact that a molecule in the true vaporous state possesses only a negligible vertical component $\mu = 1.0 \cdot 10^{-19}$ e.s.u. is at present difficult to explain. It is possible that in the vapour state the molecules exist almost entirely as doublets with the carboxyl group separated only by a small distance ca. $2 \text{ \AA.U.}$ resulting in induction between the heads and thus yielding only a small residual moment.

* Adam and Jessop, 'Proc. Roy. Soc.,' A, vol. 112, p. 370 (1926).

The Behaviour of Palmitic Acid.

The change in the surface potential² on the spreading of palmitic acid at 14.4° C. on N/100 HCl is shown in figs. 2 and 3.

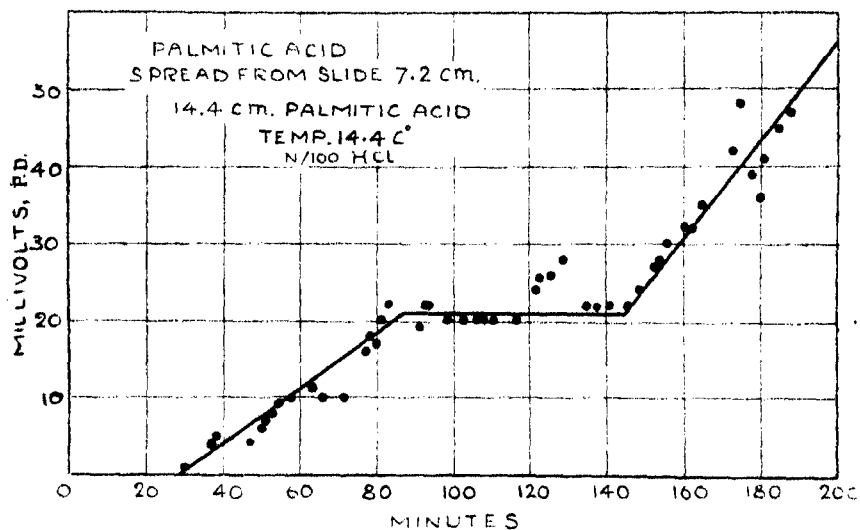


Fig. 2.

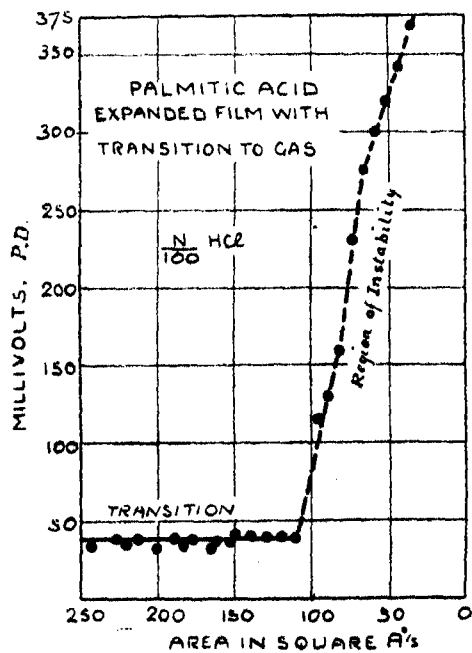


Fig. 3.

Palmitic acid at these temperatures possesses no expanded state, the F, A curves showing a direct transition from the liquid condensed to the vaporous states.

The rate of surface solution is of the order of only one-hundredth of that of myristic acid, so to increase this a glass slide exposing 14.4 cm. of interface to the water coated with palmitic acid was employed as a source. Even with this large interface the duration of each experiment was some 4 hours. The small irregularities noted in fig. 2 were found to be due to the detachment of small crystals from the large source of acid, these undergo surface solution causing a temporary local alteration in the state of the film and affect the surface potential. It was interesting to note that a small crystal detached in this manner always moved across the water surface to a position of equilibrium directly underneath the polonium coated wire, a phenomenon easily observed with pentadecylic acid crystals. The arrest points on the ΔV , time curve for spreading palmitic acid on $N/100$ HCl are found to be at 85 minutes and 145 minutes respectively. The arrest point at 145 minutes was calculated by means of calibrated solutions of palmitic acid in petrol ether to correspond to a mean molecular area of $109 \pm 3 \text{ \AA}^2$, but the area at 85 minutes was found to be more difficult to determine. From the approximate rate of the solution it was calculated to be ca. $200 \text{ \AA}^2$. With the aid of calibrated solutions the region of constant potential was found to extend quite definitely from $109 \text{ \AA}^2$ to $200 \text{ \AA}^2$, after which a small but definite fall was observed at $300 \text{ \AA}^2$ whilst at $500 \text{ \AA}^2$ the surface potential was only 11 millivolts. The difficulty in obtaining a vaporous film from evaporation of a solution in petrol ether due to the prior formation of condensed aggregates on the surface, which was noted in the case of myristic acid was found to be much more pronounced in this acid. The abrupt change in the surface potential at $109 \text{ \AA}^2$ is similar to that occurring at $100 \text{ \AA}^2$ in the case of myristic acid, and supports the view that here also there exists an intermediary liquid phase, in this case in between the liquid condensed and the homalic vaporous state, the latter consisting of horizontally inclined molecules, the electric moment being at $109 \text{ \AA}^2$ only $1.16 \cdot 10^{-19}$ e.s.u.

In fig. 3 the ΔV , area curve for palmitic acid is presented. It was found that reproducible and constant values for ΔV were obtained only for areas greater than $109 \text{ \AA}^2$ (40 mv.) where the molecules are in the vaporous state, and for areas smaller than $30 \text{ \AA}^2$ (375 mv.) in the liquid condensed state. There is evidence for the existence of an unstable expanded film as the potentials were found to be somewhat less erratic over the region $30\text{--}60 \text{ \AA}^2$ than from $60\text{--}109 \text{ \AA}^2$.

In Part III it will be shown that the molecular electric moment for a film of palmitic acid on N/100 HCl does not remain constant, but that as the film is expanded beyond the liquid condensed state the molecular moment rises until it reaches a value of $4.3 \cdot 10^{-19}$ e.s.u. at $50 \text{ \AA}^2$ and $4.67 \cdot 10^{-19}$ e.s.u. at $60 \text{ \AA}^2$ when the value of ΔV becomes too uncertain to warrant further calculations.

It would appear that a film of palmitic acid on N/100 HCl is never in a stable liquid condensed state such as exists on acid buffer solutions, but is rather in the metastable expanded state. This view is supported by the behaviour of myristic acid which has constant and repeatable values for a metastable expanded film which exists over this region.

The Behaviour of Pentadecylic Acid.

The case of pentadecylic acid proved an interesting one since at 13.4°C . its behaviour from the F, A curves is similar to that of palmitic acid, in that no expanded state exists. At 20.5°C . an expanded state is obtained. The ΔV time and ΔV area curves obtained are shown in figs. 4 and 5. It will be observed that the curve obtained at 13.4°C . (fig. 4 (a)), is similar to that obtained for palmitic acid (fig. 3), the abrupt change in potential occurring

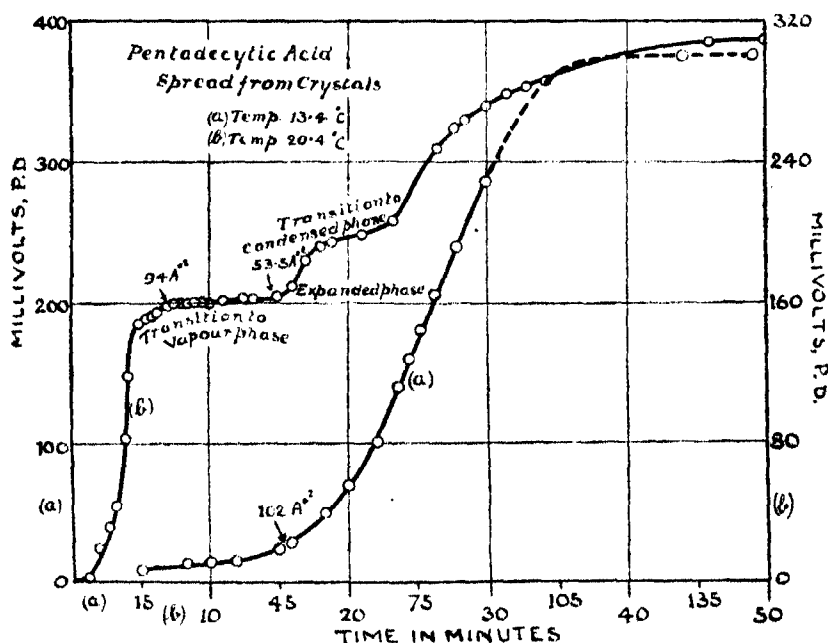


FIG. 4.

at $102 \text{ \AA}^2$ compared with $109 \text{ \AA}^2$ for palmitic acid. The curves in figs. 4, 4b and 5b are exactly comparable with figs. 3 and 4 (Part I) for myristic acid

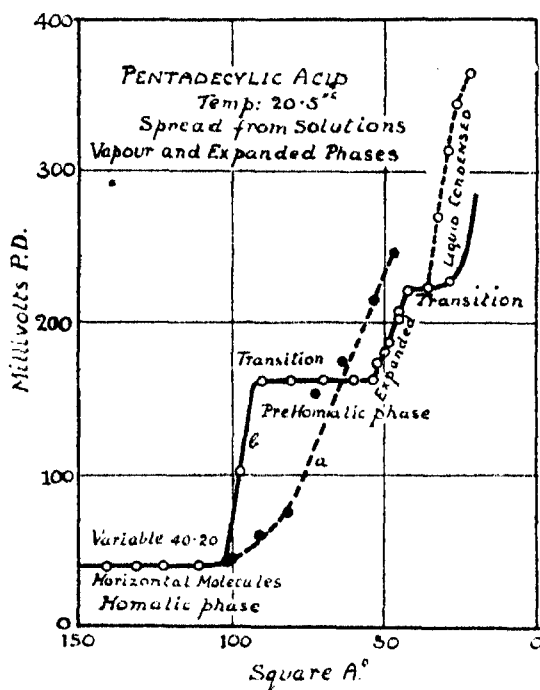


FIG. 5.

the abrupt change likewise takes place at $102 \text{ \AA}^2$ compared with $100\text{--}95 \text{ \AA}^2$ for myristic acid. These three limiting areas are close to those anticipated for the three acids in the state of closely packed horizontally inclined molecules, and lends strong support to the view that films of long chain compounds can exist in this state or phase, which we have designated the homallic state.

Pentadecylic acid possessing an odd number of carbon atoms in the chain exerts a greater equilibrium surface pressure than myristic acid, the values being 15 and 11 dynes respectively on N/100 HCl. This fact is reflected in the limiting potentials attained by the films when in equilibrium with crystals, the values being $\Delta V \propto$, 310 mv. for pentadecylic and 260-220 mv. for myristic acid.

It is here interesting to note that a film spread from an excess of petrol ether solution gives the value of 393 ± 3 mv. for both acids; the films under these conditions are in the metastable expanded state, the same is found true for palmitic acid (396 mv.).

As a result of these observations it would seem possible to suggest that a film spread from an excess of petrol ether solution of a fatty acid has the same qualities as a film obtained by quick contraction of its free area by means of slides which results, as shown, in metastable films.

Fig. 5 (a) shows that a film of pentadecylic acid at the temperature 20.5°C . has not an entirely stable expanded state, but that if no care is taken in contracting the free surface of the film, an unstable expanded film is obtained as shown in curve *a*, which compares with the curves obtained at low temperatures, fig. 4 (a).

This spreading characteristic of pentadecylic acid proves of value in comparing the results of measurements made with petrol ether solutions over the region of the expanded state and in the transition to the liquid condensed state, with those obtained by means of spreading from a crystal. It will be seen in comparing fig. 2, Part I, for the spreading of myristic acid with fig. 4 (b) for the spreading of pentadecylic acid at 20.4°C . that in the former the transition from the expanded to the liquid condensed state is not obtained owing to the low value of the equilibrium spreading pressure, but that in the latter this transition can be observed at surface potentials which correspond with those obtained by spreading with the aid of petrol ether (fig. 5b).

We may summarise the data obtained for the three acids in the following table :—

Acid.	State.	Areas in $\text{\AA}^2$.	Milli-volts.	Mean Electric moment $\mu \times 10^{18}$ e.s.u.
Myristic (Temperature $15-17^{\circ}$)	Liquid condensed	25-20.6	—	1.56 ($\bar{\mu}$)
	Transition	25-39.5	219	2.29-1.47
	Metastable expanded	39.5-ca. 22	219-396	2.29-2.31 ($\bar{\mu}=2.5$)
	Expanded	39.5-53.5	154-219	2.29-2.23
	Pre-homalic	53.5-88	154	2.23-3.6
	Homalic (vapour)	ca. 95	40 (ca.)	1.0
Pentadecylic (Temperature $21-23^{\circ}\text{C}$.)	Liquid condensed	—	—	—
	Transition	42-25	221	—
	Expanded	42-54	221-163	ca. 2.4
	Pre-homalic	54-93	163	2.4-4.02
	Homalic or vapour	102	40	1.05
Palmitic (Temperature $14-17^{\circ}\text{C}$.)	Liquid condensed buffer solutions (Part III)	—	—	1.59 ($\bar{\mu}$)
	Expanded—			
	Stable	25-60	362-360	2.5-4.7
	Unstable	60-109 $\pm$ 3	360-40	4.7-0.91
	Homalic (vapour)	109 $\pm$ 3	40	1.16

We may likewise compare these values with those calculated from the experiments of Guyot and of Frumkin.

Palmitic acid.	Myristic acid.	μ for myristic acid $\times 10^{18}$ e.s.u. at the following areas in $\text{\AA}^2$.				Observer.
ΔV in millivolts.		46.7	38.9	34.7	23.1	
390	382	2.02	2.07	—	—	Frumkin.
395	396	—	—	2.31	2.29	Guyot.
396	394	2.28	2.29	2.29	2.31	This investigation.

It will be noted that the values attained in this investigation agree closely with those calculated from Guyot's data over the region examined by that author.

The Effects of Temperature.

The effect of temperature on the interfacial potential difference for myristic acid in the transition from the pre-homalic to the liquid expanded states is very small as noted in fig. 2, Part I, a temperature rise from 15.8°C. to 21.8°C. causing only an increase in the values of ΔV from 152 mv. to 160 mv. or $1.33 \text{ mv}^\circ \text{C.}$

It was noticed that, in spite of comparative large temperature differences 14.22°C. , the area at the transitions of the expanded state remained constant to within about 1 per cent. It would seem that the variation of surface pressure, if it does not affect the mean orientation of the molecule, is not a factor which governs the surface potential. Experimental evidence tends to show that ΔV over the expanded phase is not affected to any large degree by variations in temperature, compared with the change in F with temperature as shown by N. K. Adam and Jessop.

A systematic attempt was made to obtain values of ΔV at varying temperatures, but electrical leaks across the ebonite sulphur surface due to water moisture condensation prove at present insurmountable experimental difficulties.

At first the cellar was used as an air thermostat and kept at different temperatures, and later for higher temperatures the apparatus was built into an air thermostat, but constant and repeatable results could not be obtained at temperatures higher than those mentioned above.

A Comparison between the Tilt of the Molecules and the Value of $\bar{\mu}$.

It will be seen that one obtains, except for the solid condensed phase, a characteristic vertical component of the molecular electric moment $\bar{\mu}$ for each phase independent of the number of molecules per square centimetre, *i.e.*, independent of the state of compression of the film within the region of existence of the phase, these values may be taken as follows:—

State	$\bar{\mu} \cdot 10^{-19}$ e.s.u.
Boundary of pre-homalic and homalic	3.7
Metastable and stable expanded	2.5
Liquid condensed	1.56

It appears reasonable to assume that there is no distortion or electrical interaction between the carboxylic head groups, except when the solid condensed film is subjected to pressure.

It is also possible that when the hydrocarbon chains do not interfere with one another, as for example in the highly attenuated vapour phase, induction may take place through the carboxyl heads coming into close contact (Vapour phase, Part II).

From this assumption it can readily be shown that both the values obtained of the limiting areas of existence for each phase, as well as the values of the resolved electric moments, may be accounted for on the simple hypothesis of tilting and rotation of the chain about the first carbon linkage.

In the case of the liquid condensed state, its limiting areas extend from $20.6 \text{ \AA}^2$ bounded by the solid phase, with an angle of the chain axis to the horizontal of $63^\circ 30'$ to an area of $24.4 \text{ \AA}^2$. It will be observed from the diagram (a) that this limit is imposed by simple rotation of the chain about the carbon linkage (a) giving a limiting angle to the chain axis of 47° , which gives a mean area per molecule of $25 \text{ \AA}^2$.

It can be seen, therefore, that although the tilt of the chain is varying no variation in the orientation of the carboxyl head need take place over this phase, which would explain why the vertical component $\bar{\mu}$ of the electric moment remains constant and equal to $1.56 \cdot 10^{-19}$ e.s.u. over this region of expansion. If the electric moment μ in the pre-homalic state of $3.7 \cdot 10^{-19}$ e.s.u. be the maximum value obtainable, then in this state the electric moment will make an angle of 25° with the horizontal.

The area at which the conversion of the liquid condensed phase to the liquid expanded state ends is $39 \text{ \AA}^2$, the chain axis must therefore have declined

18° in the direction of the arrow, if the carboxyl head also revolves with the chain over this 18° then we obtain a value for the vertical component of

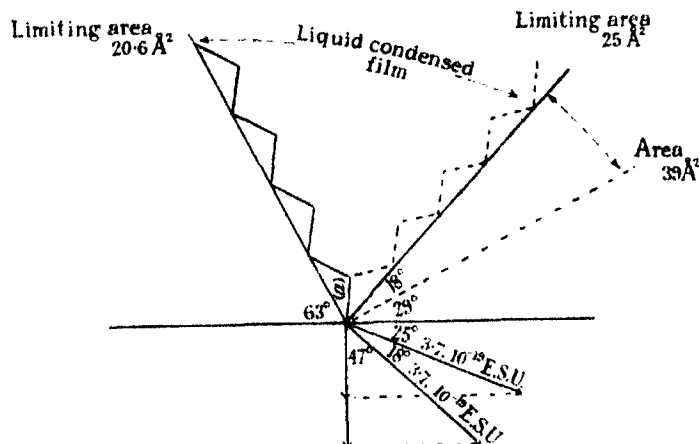


FIG. 6.—Diagram of the behaviour of a molecule in expansion of a film over the liquid condensed state and transition to expanded state (a).

the electric moment of $3.7 \cdot 10^{-18} \cos 47^\circ$ equal $2.5 \cdot 10^{-18} \text{ e.s.u.}$ which is identical with that found experimentally for the liquid expanded state.

The significance of this area of $39 \text{ \AA}^2$ which is the commencement of the transition of the liquid condensed state can be readily understood on contemplation of the mechanism of the contraction of a film over the expanded and metastable expanded regions (see later).

The range of existence of these two regions from $53 \text{ \AA}^2$ to at least $22 \text{ \AA}^2$ can be again accounted for by a simple rotation of the chain as shown in the following diagram (fig. 7).

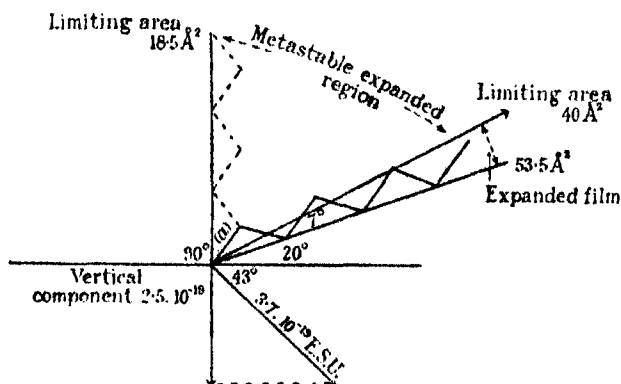


FIG. 7.—Diagram of the behaviour of a molecule in contraction of a film over the expanded and metastable expanded states.

Again we note if this hypothesis of chain rotation be adopted that the electric moment can remain constant as experimentally observed over the region of the expanded and metastable expanded films. If one contracts a film from the commencement of the expanded state at $53 \text{ \AA}^2$, as shown in Part I, fig. 4, one begins by slowly revolving the chain around the first C-C (a) linkage until at $39 \text{ \AA}^2$ the axis of the chain makes an angle of 29° with the horizontal or 29° plus $43^\circ = 72^\circ$ with the electric moment.

This angle is identical with that made by the chain axis and the electric moment in the liquid condensed state, so that at this point the molecule has two stable positions. On further contraction of the film either or both of the following rotations in the molecule may take place. One may continue to revolve the chain round the C-C linkage and so obtain a constant electric moment and a metastable expanded film (shown by curve (a) in graph 4, Part I) which may change if time is allowed into the stable configuration of a molecule in the liquid condensed film (curve (b), graph 4, Part I). Or, one may revolve by pressure the whole complex of the molecule into the liquid condensed position and thus change the moment from 2.5 to 1.56; this is shown by the true transition curve in graph 4, Part I. By too hasty a contraction both these mechanisms may take place as shown by curve (c). This clearly illustrates the inner mechanism of the hysteresis effects noticed in Part I on experiments carried out with films between the areas of $40 \text{ \AA}^2$ and $25 \text{ \AA}^2$.

A Comparison with the Electric Moments found by other Methods.

On examining the behaviour of the resolved electric moment of these acids in their various states of surface aggregation, we note that in the expanded state the value of $\mu = 2.29 \cdot 10^{-19}$ e.s.u. is obtained which includes the effect due to a double layer underneath the film, the actual value of $\bar{\mu} = 2.50 \cdot 10^{-19}$ e.s.u., being for the molecule without the contribution due to the double layer. In the liquid condensed state at a pressure corresponding to the equilibrium with the expanded state, the observed value of $\bar{\mu}$ is $1.56 \cdot 10^{-19}$ e.s.u. This value rises on further compression of the film. The maximum value of μ is found in the pre-homalic state at the moment where the expanded state is just being converted into a vapour and equal to $3.7 \cdot 10^{-19}$ e.s.u., whilst in the true vapour state the values appear to be small, of the order of $1.0 \cdot 10^{-19}$ e.s.u. at $140 \text{ \AA}^2$. Whilst these values in so far as they are attributable to the carboxyl group, must be considered as the result of replacement of a water surface by one of carboxyl groups immersed in the water yet it is interesting to compare

these values of $\bar{\mu}$ with those obtained for a carboxyl group in a non-polar environment.

No accurate values for the electric moments of the long chain fatty acids exist; data from measurements of the refraction index giving ca. $20 \cdot 10^{-19}$ e.s.u. By the more accurate method of determination from the temperature coefficient of the dielectric constant of the substance in the vaporous state or dissolved in a non-polar medium the contribution of a $-\text{COOH}$ group in ring compounds is found to be $\bar{\mu} = 9 \cdot 0 \cdot 10^{-19}$ e.s.u.; although this value due to the influence of association is naturally somewhat unreliable ('Dipolmoment und Chemische Struktur,' Debye, p. 30, Herzog, 1929). The data of Wolf* gives values for $\mu = 6 \cdot 3 \cdot 10^{-19}$ e.s.u. for isovaleric and propionic acids.

Summary.

The surface potentials of films of myristic, palmitic and pentadecylic acids on the surface of N/100 HCl have been examined for different states of the films, and the vertical component of the molecular electric moment calculated therefrom.

It is found that the values of μ obtained are dependent on the state of aggregation of the film, but are identical for the three acids in similar states of aggregation.

In confirmation of a prior prediction the value of $\bar{\mu}$ is found to be smallest and possesses a constant value equal to $1 \cdot 56 \cdot 10^{-19}$ e.s.u. in the liquid condensed state or the mesophase, and likewise to attain small values in the highly attenuated or vaporous state.

The value of $\bar{\mu}$ rises both on compression in the solid condensed state and also when the film expands into a liquid state where the molecule possesses the constant value of $\bar{\mu} = 2 \cdot 5 \cdot 10^{-19}$ e.s.u.

In the transition from the liquid or expanded state to the vapour state evidence is presented for the existence of a new phase designated the pre-homalic state appearing on expansion of a liquid phase beyond a critical area. Just before the disappearance of this phase the electric moment of the molecules in the highly attenuated expanded film attain the large value of $\mu = 3 \cdot 7 \cdot 10^{-19}$ e.s.u. Further experimental evidence is given which suggests that the molecules are horizontally orientated in the vapour state.

It is shown that a double layer caused by the attraction of ions present in the solution exists under such unimolecular films.

* 'Phys. Z.', vol. 31, p. 227 (1930).

From the knowledge that the value of the vertical component of the electric moment is constant over the region of the expanded state, a value of $\bar{\mu} = 2.5 \cdot 10^{-19}$ e.s.u. can be calculated from the slope of the curve.

This value is independent of the constitution of the substrate and is compared with those obtained from the refractive index and the dielectric constant.

On the Surface Potentials of Unimolecular Films of Long Chain Fatty Acids. Part III.—The Potentials of Solid, Liquid Condensed and Double Layer Films.

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(Received June 12, 1930.)

It was shown in Parts I and II that the vertical component of the mean molecular electric moment, $\bar{\mu}$, calculated with the aid of the Helmholtz equation $4\pi n\bar{\mu} = \Delta V$ was dependent on the state of the film.

The experiments of Lyons and Rideal (*loc. cit.*) indicated that the state of a film could be altered not only by means of the usual variables, the two dimensional pressure F , and the temperature T , but also by the extent of the adhesion of the polar group to the substrate, conveniently altered in the case of acids by a change in the p_H of the solution. That the change in this adhesion could not be attributed to the ionisation of the acid alone was shown by the fact that great changes in the stability of the film could be made over ranges of p_H well outside the range of dissociation; further for identical hydrogen ion activities the effects of different anions possessing various capillary activities were widely diverse, *e.g.*, the surface film on a citrate buffer behaves as if it were relatively more acid, and that on a borate buffer as if it were relatively more alkaline than the bulk phase.*

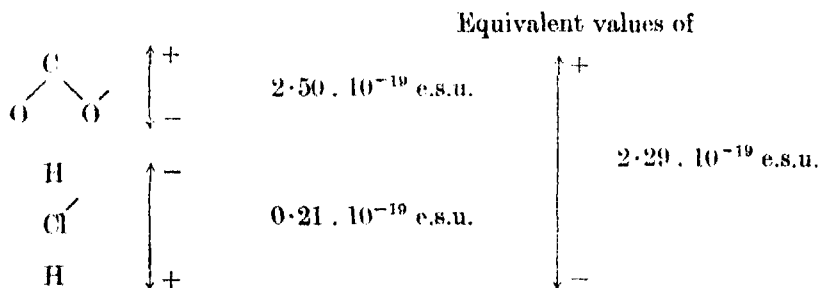
Evidence likewise from the air liquid potentials of electrolytes, as well as on the cataphoresis of air bubbles and the conductivity of the bulk phase in close proximity to a film, supports the view that underneath a film there exists a double layer consisting of anions and cations present in the electrolyte

* Cf. 'Z. Phys. Chem.,' vol. 136, p. 353 (1928); Thiel, 'Z. Elek. Chem.,' vol. 35, p. 266 (1929).

giving a contribution to the surface potential difference measured. In the absence of a film such a double layer exists at the air liquid interface of dilute soluble acids, as noted by Frumkin, but on addition of a film to the surface owing to the action of the polar groups of the film forming material the concentration of anions and cations of the solute near the surface is altered and there is thus an alteration in the double layer and in the surface potential due to the liquid alone.

In previous communications it was shown that on N/100 HC the mean value of μ for an expanded film of myristic acid as determined from the Helmholtz equation was $2.29 \cdot 10^{-19}$ e.s.u., but from the slope of the $\Delta V, n$ curve or from the equation $\Delta V_2 - \Delta V_1 = 4\pi(n_2 - n_1)\bar{\mu}$ a value of $2.50 \cdot 10^{-19}$ e.s.u. was obtained. There is thus a difference in the electric moments calculated by the two methods of $0.21 \cdot 10^{-19}$ e.s.u.

Dilute solutions of hydrogen chloride lower the surface tension of water and from measurements on the differences in air liquid potential caused by dilute solutions of this acid we may conclude that there is a preponderance of chlorine ions near the surface with hydrogen ions underneath. The general distribution of electric charge from the above measurements may be depicted diagrammatically as follows :—



The addition of a film of myristic acid in the expanded state to a surface of dilute hydrogen chloride thus not only contributes a vertical electric moment of $2.50 \cdot 10^{-19}$ e.s.u. to the interface, but brings about a change in the concentration and distribution of the underlying hydrogen and chlorine ions so that these form a new double layer differing from the original one existing at the free surface to an extent so that the air liquid potential is changed by ca. $\Delta V = 18.0$ millivolts.

From the linear character of the $\Delta V, n$ curves it is clear that the general expression for the change in potential on placing a film on the surface is

$$\Delta V = 4\pi n \bar{\mu} + \Delta V_u.$$

where ΔV_u is the change in potential caused by the film in altering the distribution of the ions in the electrolyte underneath. The value of ΔV_u in the above case = 18 mv., appears to be almost constant over the compression and expansion in which a film can exist in the same phase or state and consequently it may be inferred that the magnitude of the ionic double layer potential is determined more by the phase or state of the film rather than by the actual number of molecules per square centimetre of film-forming material. The ionic double layer underneath the film is thus much more fluid in character than the film itself, and we cannot regard each molecule in the film as having anchored beneath it a regular distribution of chlorine and hydrogen ions. For the purposes of comparison, however, it is convenient to regard the contribution of ΔV_u as, in effect, altering the mean electric moment of each molecule by a definite amount, permitting the separation of the observed value of μ into two portions, that due to the molecule itself in the film $\bar{\mu}$ and that due to the ionic double layer in the substrate $\mu - \bar{\mu}$.

Experimental.

The experimental method was identical with that described in Part I. The buffer solutions were made up according to the directions of Clark ("The Determination of Hydrogen Ions"). The palmitic acid was spread by means of a solution of freshly distilled petroleum ether from a calibrated pipette on to the solution in the trough: the film thus spread could be compressed or expanded in the usual manner by means of waxed slides. In figs. 1 and 2 are shown the surface potential differences ΔV due to the film in various states of compression on a series of buffer solutions ranging from p_H 2 to p_H 7.3, the values of ΔV_∞ or the equilibrium values being shown in the dotted curve.

It will be noted that the surface potential differences are dependent on the nature of the underlying solution even if the films be in the same phase or state and possessing identical molecular areas. At the same time the proportional surface potential increase due to compression is with the exception of the film on N/100 HCl independent of the p_H of underlying solution. We observe further that at the area of zero compression for solid condensed films (fig. 2) (ca. $20.6 \text{ \AA}^2$) a marked change in the potential gradient occurs although such is not the case at the area of zero compression for liquid condensed films ($24.4 \text{ \AA}^2$) (fig. 1). Thus on borate buffer solutions of p_H 6.8 and 7.3 where no liquid condensed or expanded phase exists on increasing the area beyond $20.6 \text{ \AA}^2$ the film becomes heterogeneous consisting of solid

patches floating on the liquid giving rise to fluctuations represented by the broken curve in the air liquid potential differences.

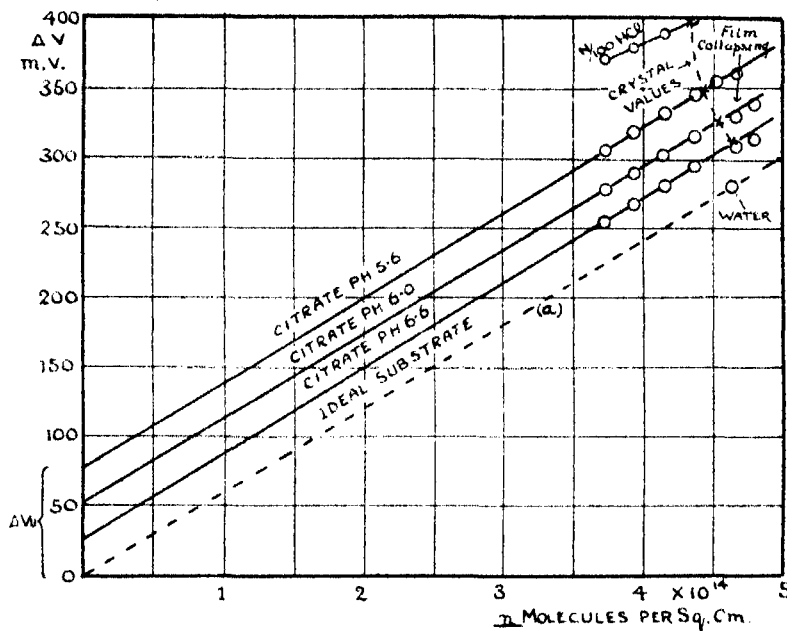


FIG. 1.

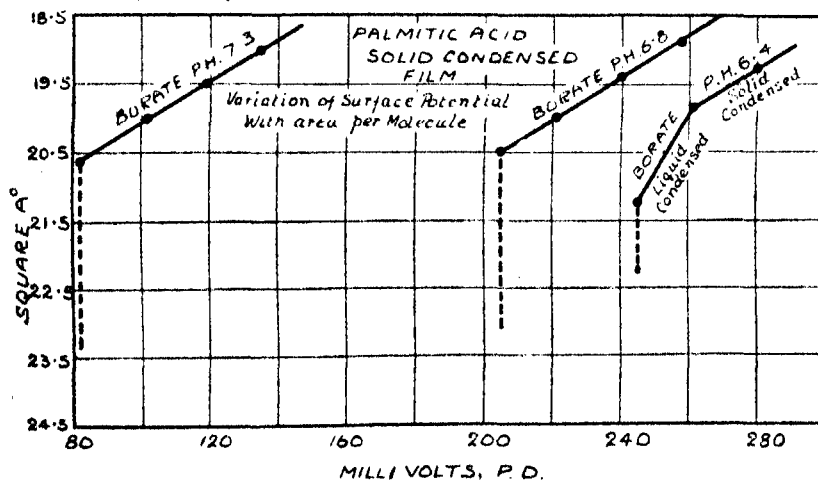


FIG. 2.

For the liquid condensed films in the smectic state, on the other hand, which do not at these low temperatures become converted into an expanded or

liquid film on increase of area, but eventually vaporise, we note that on buffer solutions no immediate change in electric moment takes place at the area of the liquid condensed film at no compression (24.4 sq. Å²).

In fig. 3 are plotted the values of the electric moments derived from I and II

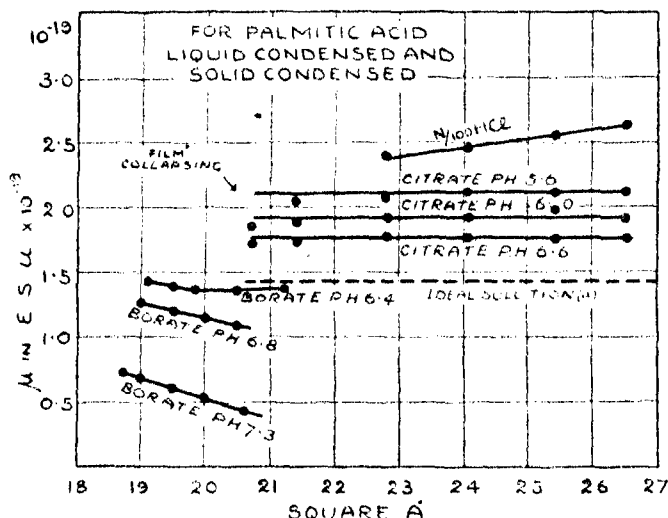


FIG. 3.

with the aid of the Helmholtz equation $\Delta V = 4\pi n\bar{\mu}$. It is seen that the electric moment μ in the liquid condensed state is practically constant on any one substrate but varies with the p_H of the substrate. In the solid condensed state there is a proportional increase in the electric moment μ as the molecules are compressed together. This increase becomes slightly greater with increasing alkalinity of the substrate, an indication that ΔV_u is altering as the adhesion of the terminal polar head to the substrate increases.

It is observed from the variation of ΔV with the nature of the substrate that the contribution of the ionic double layer to the surface potential is quite marked, and the value of the contribution of the double layer to the interfacial potential may be evaluated as we have seen from the equation

$$\Delta V = 4\pi n\bar{\mu} + \Delta V_u$$

in which $4\pi n\bar{\mu}$ is the true contribution of the film-forming material, and Δ_u the contribution of the underlying double layer to the air liquid potential difference observed. These have been evaluated in the following table:—

Acid.	State of the film.	p_H and buffer.	Mean μ e.s.u. 10^{-19}	$\bar{\mu}$ e.s.u. 10^{-19}	ΔV_u millivolts.
Myristic	Expanded	2 N/100 HCl	2.29	2.50	- 18
Palmitic	Liquid condensed	5.6 citrate	2.06	1.59	+ 78
	" "	6.0 "	1.86	1.59	+ 53
	" "	6.6 "	1.71	1.59	+ 25
	Solid condensed	ca. 7.0 water	1.59	1.59	0
	" "	6.8 borate	---	3.18	-378
	" "	7.3 "	---	3.18	-498

It will be noted that the value of $\bar{\mu}$ the actual contribution of the molecule to the surface potential apart from the contribution of the underlying ionic double layer, is in the liquid condensed state constant and equal to $\bar{\mu} = 1.59 \cdot 10^{-19}$ e.s.u. over the p_H range 5 to 7 on citrate buffer solutions. The contribution of the ionic double layer is, however, more variable, ranging from +78 mv. at p_H 5.6 to +25 mv. on a buffer solution of p_H 6.6. From fig. 4 the difference in capillary activities of the borate and citrate ions is clearly observed.

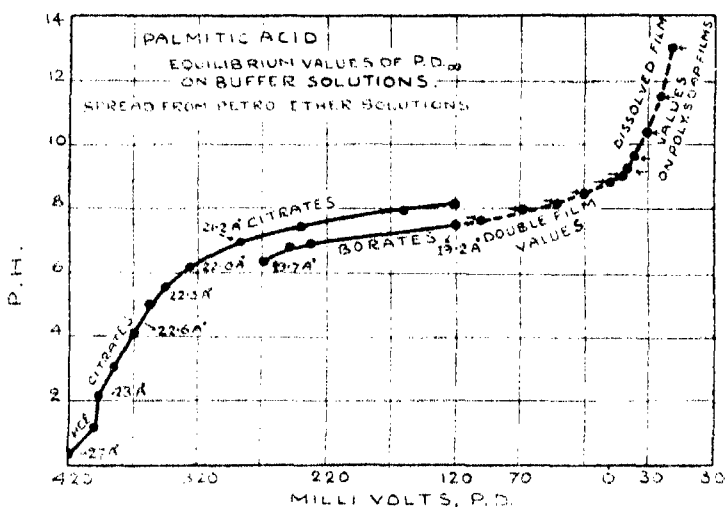


FIG. 4.

We may conclude that the value of μ calculated from the apparent surface potential change

$$\Delta V = 4\pi n\mu$$

is dependent on :—

- (1) The hydrogen ion concentration of the underlying surface layer, which differs from that of the bulk phase.
- (2) The character of the anion in the solution and its capillary activity.
- (3) On the phase of the film ;

Source of water.	$4V_{\alpha}$ in millivolts.
Distilled from quartz	260
Distilled "	280
Distilled from block tin	302
Ordinary distilled water	345

These wide variations in ΔV_{∞} , which we have seen are to be ascribed partly to a double layer underneath the film, would give rise to wide variations in the cataphoretic velocity of film particles, and a high conductivity in the liquid in a direction parallel to the film surface, as noted by McBain and Peaker (*loc. cit.*).

In fig. 1 (graph *a*) are shown the surface potential values of a film of palmitic acid calculated from the constant moment $\bar{\mu} = 1.59 \cdot 10^{-19}$. This should give the surface potentials of a liquid condensed film under compression on a substrate which can give no variations due to the ionic double layer. It is interesting to note that the crystal equilibrium surface potential value for palmitic acid on water at approximately p_H 7 of 280 mv. gives a value on this curve for the area of ca. $21 \text{ \AA}^2$ which is in close agreement with that found from the spreading pressure and area measurements made with the aid of the Langmuir trough.

Multimolecular Film Formation.

In a previous communication (Lyons and Rideal) it was shown that on solutions more alkaline than p_H 8 a film of palmitic acid commenced to undergo surface solution, but that after part of the film had undergone solution the remainder appeared to be insoluble. This phenomenon was ascribed to the formation of a double film, the molecules of the dissolving soap coming up to the surface underneath the superficial film. It was suggested that the structure of the double film thus formed was similar to that of the elementary bimolecular leaflet of a soap bubble. If a crystal of palmitic acid be placed upon the surface of water more alkaline than p_H 8 a unimolecular film is rapidly formed, but this is finally converted into the more stable bimolecular leaflet; this whole process takes place in a period of some 10 to 30 minutes.

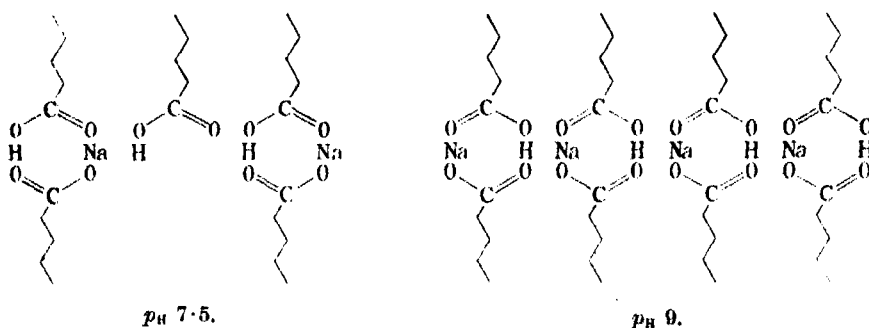
It is evident that if the bimolecular film consists of a doubly orientated layer of sodium acid palmitic or sodium palmitate the system should be completely symmetrical, and the double film should not make any contribution to the surface potential.

It was considered of interest to examine this phenomenon of surface solution and bimolecular film formation by the method of surface potentials.

It was found that at p_H 8 on citrate buffers and at p_H 7.5 on borate buffers solution of a palmitic acid film on the surface takes place, and the potential falls taking up after a few minutes a constant value, there remaining still a solid film on the surface. At p_H 9.0 the final potential acquired, although there is still a film on the surface, is found to be $\Delta V = 0$ (fig. 4). Thus over the region of p_H 7.5 to p_H 9 on a borate buffer the value of ΔV is gradually

sinking, and at the same time the surface solution is increasing. It is probable that at p_H 9 the surface film is a completely symmetrical bimolecular layer of sodium acid palmitate thus contributing no electric moment to the surface. On solutions less alkaline, the positive values of ΔV when considered in the light of the experiments on the solution of films indicate that the top layer still consists of a completely packed unimolecular film with the lower layer less sparsely packed.

Diagrammatically we may represent the structures of these films from p_H 7.5 to p_H 9 on borate buffers as follows :—



As the alkalinity is raised above p_H 9 the surface spreading pressure becomes too small to form a continuous film of acid without surface solution occurring, and the subsequent formation on the surface of a layer of sodium palmitate to which, as Guyot showed, the negative values are due. As the composition of the upper layer becomes richer in sodium palmitate so does the solubility of the material increase, until at ca. p_H 10.5, and in solutions of higher alkalinity, the surface phase scarcely changes at all, but consists essentially of a film of sodium palmitate with a less densely packed sheet of sodium palmitate underneath it, similar to the acid soap films at p_H 7.5. This change is confirmed by the observations of Miss Laing on the analysis of soap films; she found that the constitution of films made from solutions between p_H 7-9 consisted of sodium acid palmitate, and films made from solutions of greater alkalinity than p_H 9 consisted only of sodium palmitate.

Since the bimolecular film between p_H 9-13 is relatively stable it appeared possible to build up a series of sheets of bimolecular film, each sheet contributing nothing to the interface potential, on the top of a substrate of sodium palmitate present on the surface due to the operation of surface forces in accordance with the Gibbs equation.

This state of affairs can be pictured as follows :—

It has in fact been found possible in the following manner to realise this experimentally, and to build up a thick tenacious transparent film or glaze possessing an identical electric moment to that of a unimolecular film on solutions lying between p_H 9 and 13 in alkalinity.

A quantity of palmitic acid in petrol ether sufficient to form two unimolecular films of area $20 \text{ \AA}^2$ per molecule was placed upon the surface of a borate buffer at p_H 10.

The lower curve in fig. 5 shows the process of solution by the fall in potential to form a Gibbs adsorbed layer, which took up a constant value of -30 mv. Additional palmitic acid in petrol ether was then placed on the surface. This spread on the surface to form a thick glaze which took up a value of nearly $+40 \text{ mv.}$ On disappearance of the glaze and conversion of the acid into sodium palmitate, the surface potential changed until it came to the constant value of -30 mv. characteristic of the original Gibbs layer, but there was now a thick clear film on the surface.

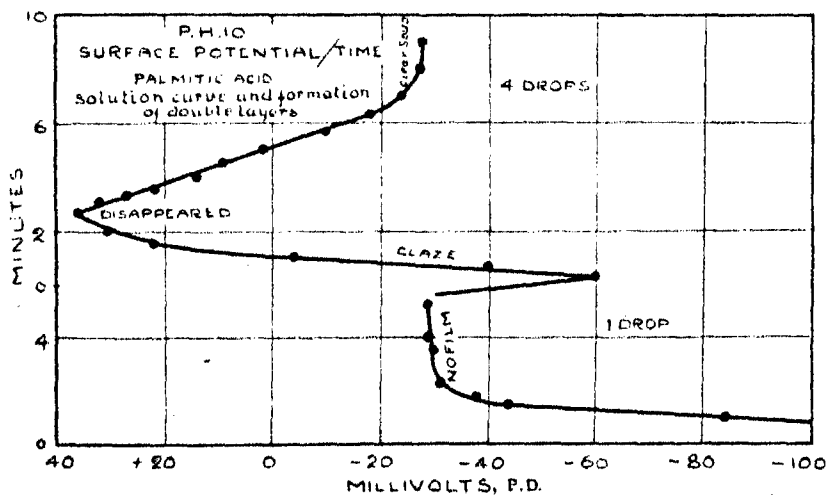
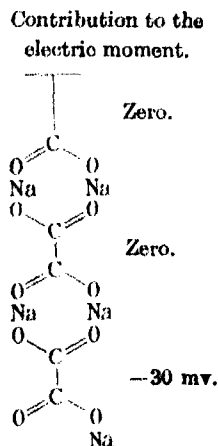


FIG. 5.

By increasing the alkalinity of the underlying solution similar results can be obtained, the chief difference being the increased rates of solution and the weakening of the protective influence of the adsorbed Gibbs layer on the

thick bimolecular films above it. But in all cases the potential of the final thick film was identical with that of the Gibbs layer regardless of the thickness of the former. Thick films up to ca. 16 molecular thicknesses have been built up in this way by further addition of palmitic acid.

Summary.

The surface potentials of films of palmitic acid have been examined on substrates of various hydrogen ion concentrations. It is concluded that below the surface film there exists an ionic double layer which makes an effective contribution to the interfacial potential. The vertical component of the electric moment of palmitic acid in the liquid condensed state is found to be constant and equal to $1.59 \cdot 10^{-19}$ e.s.u. regardless of the acidity of the substrate, the apparent electric moment, however, may vary from ca. $2.06 \cdot 10^{-19}$ e.s.u. to ca. $1.7 \cdot 10^{-19}$ e.s.u. due to the effects of the underlying ionic double layer. The effects of the ions borate and citrate of different capillary activities on the ionic double layer is found to be marked.

Similar effects are noticed in the molecule on compression of a film in the solid condensed state where $\bar{\mu} = 3.18 \cdot 10^{-19}$ e.s.u.

On alkaline solutions the interfacial potential difference falls to small values and attains negative values on strong alkali. It is shown that bimolecular leaflets possess an effective moment of zero confirming the structure attributed to the elementary leaflets of soap bubbles and multimolecular layers up to 16 molecules thick with zero effective moment have been prepared in the form of transparent tenacious glazes.

On the Eddy System in the Wake of Flat Circular Plates in Three Dimensional Flow.

By DOROTHY MARSHALL and T. E. STANTON, F.R.S.

(Received October 23, 1930.)

[PLATES 4, 5.]

The method of colour bands for revealing the characteristics of the motion of water was first used by Osborne Reynolds some 50 years ago in the determination of the critical velocity at which the streamline motion in parallel pipes broke down. Since that time several attempts have been made to use the same method for the study of vortex motion, but owing apparently to lack of sufficient precautions to ensure that all internal motions in the reservoir supplying the stream had disappeared before the experiments were made, the success achieved has not been as great as might have been expected.

In 1910 a small water channel consisting of a rectangular canal 3 inches wide and 4 inches deep by 10 feet in length was constructed at the National Physical Laboratory for the study of the flow round plates and models and the results of a series of experiments made in the channel were described by Mr. C. G. Eden in his paper communicated to the Advisory Committee for Aeronautics.* The flow in this channel, however, was not altogether satisfactory for although the initial disturbances in the water supply were reduced by means of baffle plates and the use of a large supply tank, so that no eddies were present, there were indications that the direction of motion at any point was not independent of the time. The information obtained by Mr. Eden with this channel was of considerable value in revealing the nature of the flow in the wake of inclined plates and streamlined models.

The first water channel made for the present series of experiments was made on the lines of Reynolds' original apparatus and consisted of a horizontal glass-sided tank, 12 feet long, 2 feet deep and 1 foot 6 inches wide. Inside this tank about 6 inches from the bottom was supported a horizontal glass-sided water channel of internal section 1.5 inches by 1.5 inches having a bell mouth piece at one end and an outlet regulated by a cock at the other end.

On opening the cock, water was drawn through the channel from the supply outside it, the outlet from the colour reservoir being situated a few inches in

* Reports A.C.A., 1910-11, p. 48, and 1911-12, p. 97.

front of the bell mouth piece so that the stream from it was drawn into the channel under the same head. Considerable difficulties were encountered in obtaining a state of steady flow down this channel such that the colour band was always accurately situated at its axis, although when the square channel was replaced by circular glass tubes there was no difficulty in repeating the experiments of Osborne Reynolds on the critical velocity in pipes. It was thought at first that the lateral shifting of the colour band might be due to want of uniformity in the temperature of the water in the tank or small differences between the density of the water and that of the colour solution, and some time was spent in improving these conditions. No substantial improvement resulted and it was concluded that the tank was not sufficiently large to give equality of head in the approach streams.

For the above reasons, further work on this channel was discontinued and since previous experience had shown that symmetrical steady motion in a water channel was more easily set up when the motion was vertical instead of horizontal, an attempt was made to overcome the practical difficulties (due to pressure) inherent in the construction of a vertical water channel with glass sides. The channel constructed on these lines is illustrated in fig. 1.

The cast-iron supply tank for this channel was 3 feet by 3 feet by 3 feet, and had a plate-glass front $\frac{3}{8}$ -inch thick. The channel was constructed of wood $1\frac{1}{2}$ inches by $1\frac{1}{2}$ inches inside and was about 10 feet long. This was fitted into the base of the tank with a bell mouth piece projecting about 8 inches from the floor. The lower 5 feet was provided with glass front and back for observational purposes. The mean rate of discharge was measured by measurement of the outlet water.

For examining the motion of the water in the channel, the colour was in the first instance introduced into the region of the approximately still water above the mouth piece, as is customary in this work. In order to ensure that the colour solution was at the same temperature as the water in the reservoir, an intermediate colour receiver was used which was completely immersed in the water.

In this method it is very difficult to introduce the colour into the main mass of water without causing some slight disturbance which affects appreciably the formation of the stream lines, and finally the device was adopted of a colour reservoir consisting of a vertical tube open to the atmosphere discharging into the supply tank under gravity and of such a section as to give a colour stream of the dimensions required. In this way, the descent of the water in the tank caused a corresponding flow of colour into the still water with the

minimum disturbance. This was a great improvement on all the methods of colour introduction previously tried, although for the reasons given below it

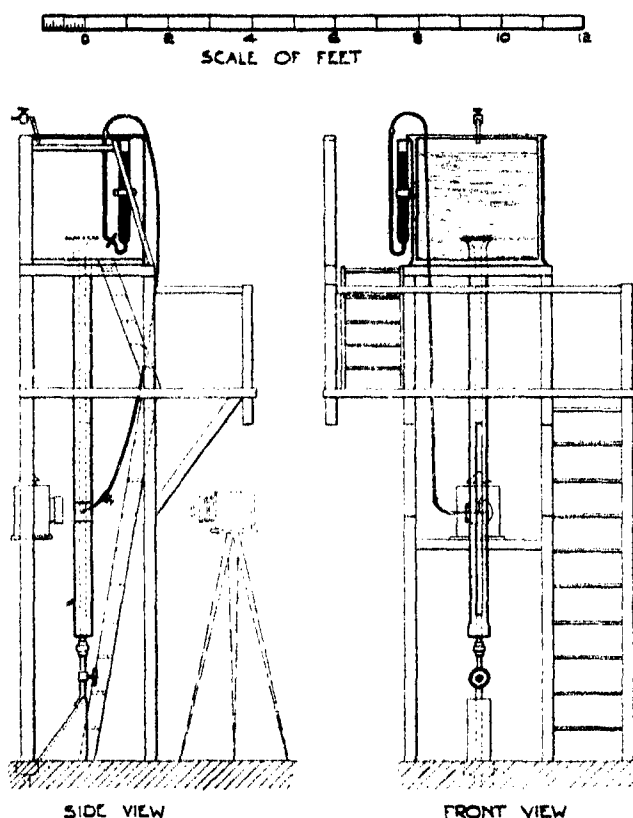


FIG. 1.—N.P.L. 1·5-inch Square Vertical Water Channel.

did not prove satisfactory for the particular purpose of the present experiments.

Some preliminary experiments were then made with a thin brass disc 7·5 mm. diameter placed in the axis of the channel normal to the flow and supported from below by a spindle of small diameter. On attempting a visual examination of the flow round the disc by means of the colour stream, it was found to be extremely difficult to ensure that this stream impinged symmetrically on the disc. At low speeds the existence of a permanent vortex ring behind the disc was clearly demonstrated, but this was invariably lop-sided. Considerable time was spent in trying to obtain an axial impingement of the colour stream, but without success, and finally it was decided to abandon temporarily the introduction of the colour into the still water of the tank and to introduce it

through the vertical supporting stem of the disc to the centre of the upstream face. This constituted a marked improvement, but there was still trouble in obtaining a uniform radial flow outwards to the edge. This difficulty was finally surmounted by using two thin parallel discs very close together and allowing the colour to flow radially outwards in the space between them. The state of motion obtained in this manner proved very suitable for the study of the eddy motion subsequently developed, the only objection being that the combination of the two parallel plates could no longer be regarded as a thin plate, the ratio of thickness and diameter being about 0.1. The general dimensions of the plate and supporting spindle will be seen from photograph No. 1 which was taken at zero velocity.

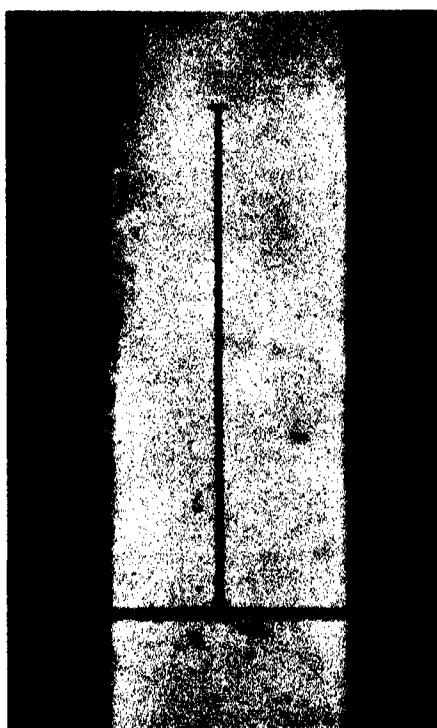
Experiments with Circular Plates.—A series of experiments was then made on circular discs of diameters 3, 4, 5 and 6 mm. Photographs of the eddy system in the wake were taken at various mean speeds of flow in the channel, and for each condition of flow the periodicity of the eddies in the wake was taken by a stop watch.

The nature of the motion in the wake of the discs was as follows. At low speeds of flow between an upper well-defined limit given by $vd/\nu = 195$ and a lower limit not well defined, probably on account of experimental difficulties, but of the order of $vd/\nu = 5.0$, a permanent vortex ring was developed at the rear of the disc having an external diameter greater than that of the disc, as will be seen from a comparison of photographs 2 and 1 (Plate 4).

The circulation of the fluid in the vortex ring was apparent visually, but is not seen in the photograph. The existence of a vortex ring at the back of a circular plate was first pointed out by Osborne Reynolds in 1877 in a lecture on Vortex Motion at the Royal Institution.

On the flow exceeding the upper limit, an oscillating disturbance of the vortex ring became apparent, with the result that successive portions of its substance were discharged downstream at regular intervals of time depending on the rate of flow and the dimensions of the disc. The appearance of these vortices will be seen from photographs Nos. 3, 4 and 5 (Plates 4, 5). This state of flow corresponds to that observed by Eden in the case of inclined square plates.* The phenomenon could not be described as a shedding of the vortex ring as a whole, the impression derived from visual observation being that at the upper critical speed the inward pressure gradient in the ring became inadequate for its maintenance, with the result that the outside portions of the ring in contact with the fluid streams from up stream became detached.

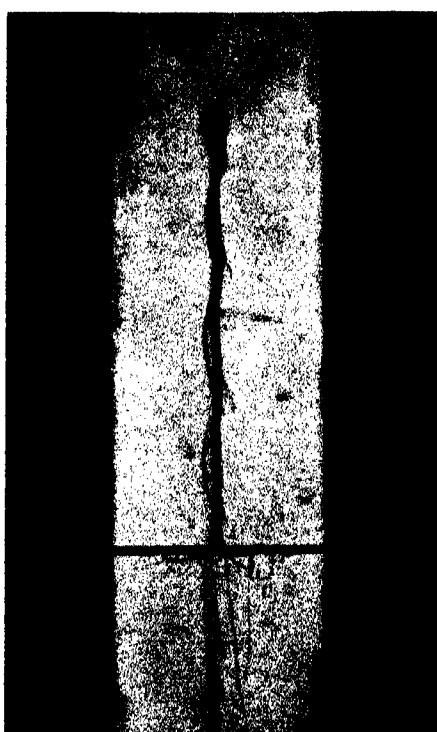
* Report A.C.A., 1911-12, figs. 16 to 20.



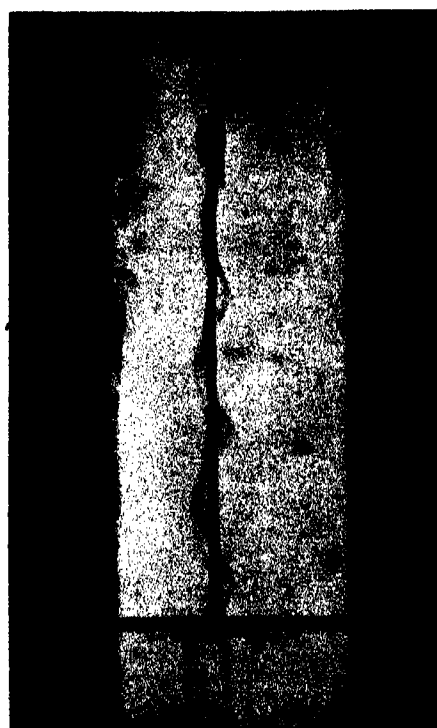
No. 1 (83)
3 mm. disc.
Velocity zero.



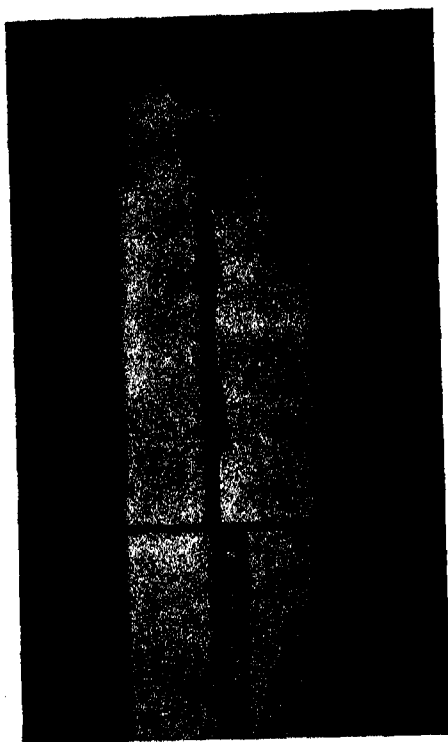
No. 2 (84)
3 mm. disc.
Velocity 5.7 per sec.



No. 3 (89)
3 mm. disc.
Velocity 7.3 cm. per sec.



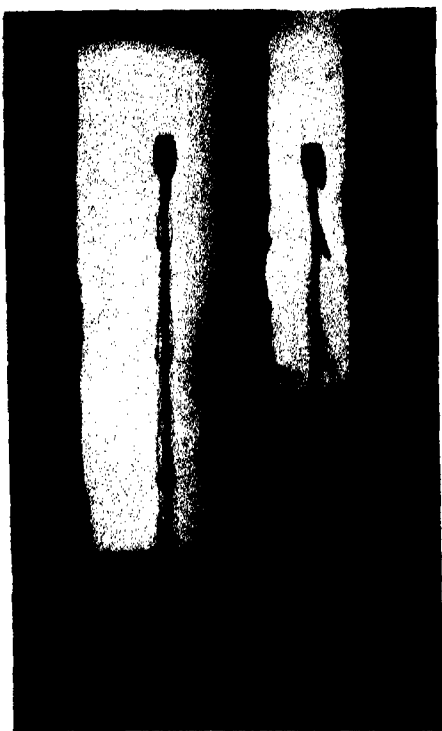
No. 4 (85)
3 mm. disc.
Velocity 7.6 cm. per sec.
(Facing p. 298)



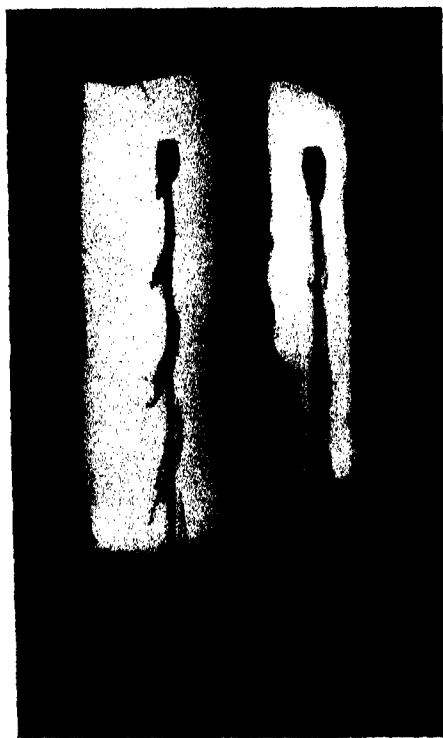
No. 5 (136)
5 mm. disc.
Velocity 2.6 cm. per sec.



No. 6 (294)
3 mm. disc.
Velocity 9.6 cm. per sec.



No. 7 (301)
3 mm. disc.
Velocity 7.75 cm. per sec.



No. 8 (291)
3 mm. disc.
Velocity 8.45 cm. per sec.

The difficulties in the determination of the lower limit of flow for which a permanent vortex ring appeared to be stable lay in the extremely low speed of flow at which the change from vortex motion to stream line motion took place, which for a 5-mm. disc appeared to be of the order of 0.1 cm. per second.

It was, of course, quite easy to regulate the discharge from the 1.5 inches by 1.5 inches channel to give a mean speed of this value, but owing to the possibility of small differences in the temperature of the water producing regional up currents the actual speed at the disc was conjectural.

All that can be said is that at this apparent speed the coloured water behind the disc presented the appearance of continuous stream lines concave to the walls of the channel, in contradistinction to the greater curvature and the convexity to the walls of the boundary layer of the vortex ring.

It may be noted however that even at the lower limit the velocity is still considerably above that which would make vd small compared with ν , which is the condition that the nature of the flow should be calculable from the hydrodynamical equations with the inertia terms neglected.*

To determine the critical value of vd/ν at which the periodic vortices were discharged, careful observations of the critical speed were made for the different sizes of discs used. The stream line flow in the channel was approximately parabolic in character and the velocity of approach of the water to the disc was calculated from the mean flow multiplied by an experimentally determined constant, the value of which was somewhat greater than 0.5. The characteristics of the flow at the critical speed are given in the following table.

Table I.—Experiments at the Critical Velocity.

Diameter of disc.	Velocity of approach of stream (V).	Periodicity of eddies discharged (T).	Value of vd/ν .	Photograph number.
mm.	cm./sec.	seconds		
3.0	7.3	0.35	200	89
4.0	5.4	0.61	197	137
5.0	4.2	0.93	191	136
6.0	3.6	1.34	199	153

It appears therefore that the periodic discharge begins at a definite value of vd/ν , which is approximately 195. The dynamical similarity in the motion of the eddies at the critical speed is well brought out from the values of the

* Lamb's "Hydrodynamics," 4th ed., p. 588.

periodicity which are closely proportional to the squares of the diameters of the plates. It may be remarked that, although the velocity at which the eddy discharge commenced was definite, this motion did not appear in a full-blown manner but as illustrated in photograph No. 5, in which the incidence of the motion was detected.

The photographic apparatus originally set up for the purpose of the investigation was only capable of giving views of the flow projected on one plane which was parallel to the plate-glass front and back of the channel. From visual observation of the manner in which the coloured fluid was detached from the disc and also from the appearances of the photographs, especially Nos. 3 and 4, it was thought at first that the wake consisted of a spiral vortex continuously unwound from the edge of the disc, and corresponding with the hypothetical case investigated by Levy and Forsdyke,* who have obtained expressions for the axial and rotational velocity of a helical vortex in the wake of a surface of revolution moving in a fluid in the direction of its axis. This assumption was made in a preliminary note communicated to the Aeronautical Research Committee early in the year on the results of the observations, but it was pointed out on that occasion by Dr. L. Rosenhead, to whom the note had been submitted, that there were strong theoretical reasons against such a conclusion and that the probable interpretation of the photographs was the periodic discharge from the disc of a series of rings of vorticity.

It was decided that further investigation was necessary in order to clear up this point, and as it appeared probable that simultaneous views of the wake in two planes at right angles might furnish conclusive evidence, an attempt was made to obtain them. The apparatus set up for this purpose is illustrated in fig. 2. New windows were inserted in the sides of the water channel, and, by means of the arrangement of lanterns and mirrors shown, satisfactory photographs of the wake projected on two planes at right angles were obtained. From the results of a large number of exposures it was found that each photograph fell into one of two categories, the one illustrated in photograph No. 6 and the other in photographs Nos. 7 and 8 (Plate 5). The series of which photographs Nos. 7 and 8 are typical appear to demonstrate with reasonable certainty the accuracy of Dr. Rosenhead's conclusions as to the nature of the wake, the view to the right in No. 7 and to the left in No. 8 being in the plane containing the axis and the point at which the vorticity begins to be shed from the disc. The second series of which photograph No. 6 is typical are views

* 'Proc. Roy. Soc.,' A, vol. 120, p. 670.

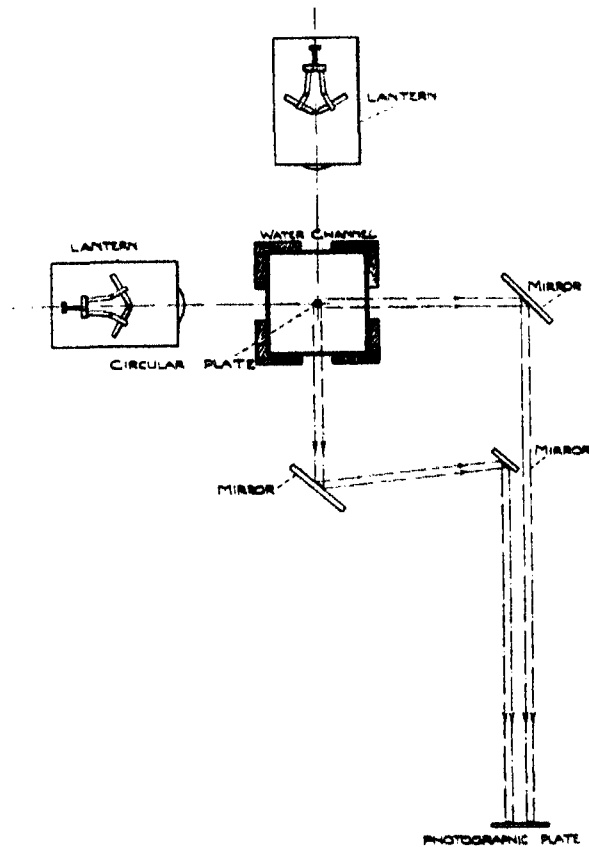


FIG. 2.—Method of obtaining Simultaneous Photographs of the Motion in Two Planes at Right Angles.

on planes which have a considerable inclination to the above-mentioned plane so that the views presented are composite views of the two main aspects of the ring.

*The Isotopic Constitution and Atomic Weights of Zinc, Tin,
Chromium and Molybdenum.*

By F. W. ASTON, F.R.S.

(Received November 24, 1930.)

Introduction.

In a previous communication* a method of photometry of mass-spectra was described by which the relative abundance of isotopes could be measured. The accuracy of the method was shown to be amply sufficient for a preliminary survey of complex elements with a view to finding out any simple laws, if such existed, governing relative abundance, and for checking atomic weights measured by more usual ways. The following is an account of further experiments made by means of the same apparatus and general method.

The sequence in which the elements are investigated is affected by considerations of many kinds. In seeking relations between abundance ratios one naturally selects the most complex element which can be easily handled and avoids the examination, immediately after, of another which has isobaric lines. After the completion of the work on krypton, xenon and mercury already published (*loc. cit.*) zinc was successfully investigated. Following zinc an attack on cadmium was planned for which purpose a sample of pure cadmium methyl had been specially prepared. Cadmium methyl has a strong chemical similarity to zinc methyl and was expected to behave in much the same way in the discharge. Actually this is far from being the case. No trace of the cadmium lines could be detected whether the vapour of the compound was admitted pure or diluted with other gases. A few weeks later a second attempt was made but resulted like the first, simply in deposition of cadmium on the walls of the discharge bulb completely upsetting the normal beam of rays. Finally a special arrangement was made by which the vapour was admitted at the anode end of the bulb, in the hope that this would lessen the disturbance near the cathode. This procedure was equally unsuccessful and as no more stable volatile compound of cadmium seems available this element will presumably have to be investigated by the much more difficult technique of "anode rays" by which its isotopes were first observed. This failure is particularly unfortunate, as the remarkable similarity between the

* 'Proc. Roy. Soc.,' A, vol. 126, p. 511 (1930).

isotopic groups of cadmium and tin had already been noticed and commented upon.*

After the first failure with cadmium, tin was satisfactorily investigated and since the last traces of the zinc spectrum had now disappeared from the discharge conditions were suitable for work with germanium. The compound available was germanium ethyl which had been used in the discovery of the eight isotopes of this element.† Quantitative measurement is, however, a problem very different from mere identification and, owing to its instability and the liberation of inconvenient quantities of hydrogen by this compound when long exposures were attempted, no results were obtained which could be regarded as entirely satisfactory. After some weeks of fruitless work it was decided to postpone further work on germanium until the methyl compound could be obtained which, there was reason to hope, would prove more favourable. The welcome arrival of a volatile compound of chromium and later one of molybdenum directed attention to these elements which were then investigated with satisfactory results.

Experiments with Zinc.

The compound zinc methyl was employed and as its boiling point is very low (46° C.) the liquid was cooled in melting ice and its vapour admitted to the discharge tube through a fine leak. It was soon clear that the secret of obtaining strong zinc lines was to have nothing but the vapour of the methyl present. The presence of other elements more easily ionised or capable, from any other cause, of carrying the current more easily seems to act adversely. Doubtless the many earlier failures to get zinc lines were largely due to the presence of mercury. The low ionisation potential and abnormally great "current carrying" power of this element appear to enable it to suppress the mass-spectrum of zinc entirely, although the partial pressure of the latter is far the greater.

Even under the best conditions the zinc lines are far from strong, so rather larger slits than those used for xenon were employed, this being justified by the relatively wider spacing of the lines. It was necessary to give exposures of 30 to 45 minutes to get measurable effects from the line of the faintest isotope Zn^{70} which is present to less than 1 per cent. The wide spacing of the zinc lines enables the method of "intermittent exposures"‡ to be applied as with krypton and useful additional confirmatory results were obtained by comparing

* Aston, 'Phil. Mag.', vol. 49, p. 1191 (1925).

† Aston, 'Nature', vol. 122, p. 167 (1928).

‡ See 'Proc. Roy. Soc.,' A, vol. 126, p. 517 (1930).

spectra taken with exposures of *e.g.*, 16, 8, 4 minutes and drawing the curve of log. line intensities. The three principal isotopes 64, 66, 68 form about 90 per cent. of the element, so that the error in determining the mean mass number depends almost entirely on fixing their two ratios of abundance. These were therefore determined with the highest accuracy feasible. The ratios between the weaker isotopes are approximate only.

Packing Fraction of Zinc.—In the general curve* of the elements this quantity is at a minimum in the region of zinc which was expected to give a value of about -10 like nickel. At the time the first successful analysis of zinc by the mass-spectrograph was made† many attempts were made to measure its packing fraction, but with no success. The principal difficulty is to introduce known masses suitable for comparison into the discharge and still retain a controllable intensity of zinc lines. On the present occasion advantage was taken of the following facts.

As is well known, the discharge tube under normal conditions contains carbon and its compounds with hydrogen derived from the wax joints and tap grease and these give two well-marked groups of lines, the C_1 group 12, 13 ... , and the C_2 group 24, 25 ... , which were and still are of prime importance in calibration of the mass scale. No evidence of groups containing more atoms of carbon than two was obtained, on mass-spectra, until recently when on a spectrum from the discharge in nickel carbonyl some of the lines of a C_3 group 36, 37 ... were faintly but clearly visible.

When the tube had been running for a long while with nothing but zinc methyl passing and had reached steady conditions, spectra obtained with fairly long exposures all showed not only the C_3 group but, rather fainter, the C_4 group. In the former the line $39\ C_3H_3$ is the strongest, in the latter line $50\ C_4H_2$. Why these molecules appear when metallic compounds are used and why they are produced in these proportions, or indeed at all, in the discharge are problems worth a special research and need not be further discussed here. The importance in the present work is that their identity seems beyond dispute, so that they provide the necessary standards for the determination of the packing fraction of zinc, and by good fortune the ratios $39:50$ and $50:64$ are near enough for that purpose. It was not easy to get brackets of the right intensity neither were the wide slits suitable for this measurement, in fact only one plate could be regarded as really satisfactory, this gave

$$\text{Packing fraction of } Zn^{64} = -9.9.$$

* See 'Proc. Roy. Soc.,' A, vol. 123, p. 380 (1929).

† Aston, 'Nature,' vol. 122, p. 345 (1928).

This can only be regarded as a provisional value but it is in excellent agreement with that expected from the curve.

Zinc Results.

Mass numbers of isotopes	64	65	66	67	68	69	70
Log reciprocal line intensity	0	1.29	0.287	0.98	0.487	1.81	2.15
Relative abundance $Zn^{64} = 100$	100	5.2	53.95	11.2	35.73	1.7	0.8
Percentage abundance	48.0	2.5	25.0	5.3	17.1	0.85	0.38

These values give for zinc the same isotopic moment as mercury 1.41 and a mean mass number of 65.45_2 . Subtracting 0.065 for the packing fraction and 0.007 for change to the chemical scale we get

$$\text{Atomic weight of zinc} = 65.38_0 \pm 0.02.$$

A value in exact agreement with the best chemical determinations.

In the first description of the mass-spectrum of zinc (*loc. cit.*) the order of intensity of the two weakest isotopes was given incorrectly. The reason for this was that germanium—which contains an isotope 70—had been used immediately before and was still present in the tube so that, except proving that it was less intense than Zn^{65} , no evidence either for the abundance, or indeed for the existence of Zn^{70} could be safely drawn from the mass-spectrum. On the other hand the curve given earlier by Dempster* showed a well-marked hump at 70 and none at 69. It was, therefore, naturally assumed that 70 must be more abundant than 69, hence the order of intensity then given. This discrepancy between the abundances suggested by Dempster's curve and those now measured is considerable and has no obvious explanation, but the consistent photometry of the group of lines on all of a very large number of plates and the agreement with the chemical atomic weight leave little doubt that the results of the mass-spectrograph now given are substantially correct.

Experiments with Tin.

This element was investigated as usual by means of its methyl compound. It is the most complex of all yet analysed having no less than 11 isotopes. The mass numbers of these are too close to permit of the use of the method of intermittent exposures, but their number and wide range of abundance are favourable for the method used for xenon and mercury (*loc. cit.*). Even with these advantages it was found very difficult to maintain the discharge sufficiently constant over the long exposures necessary to record the fainter lines. A great

* A. J. Dempster, 'Phys. Rev.', vol. 20, p. 635 (1922).

many plates were taken before a satisfactory series of exposures of 20, 10, 5, 10, $2\frac{1}{2}$, 5 minutes was obtained. From the log curve drawn reasonably consistent values of the ratios could be deduced. As an additional check spectra containing both tin and xenon lines taken some years before were measured up photometrically and found to give ratios not inconsistent with the newer ones.

Tin Results.

Mass numbers of isotopes	112	114	115	116	117
Log reciprocal line intensity	1.36	1.53	1.66	0.28	0.43
Relative abundance $\text{Sn}^{120} = 100$	3.98	2.75	1.62	52.48	36.31
Percentage abundance	1.07	0.74	0.44	14.19	9.81

Mass numbers of isotopes	118	119	120	121	122	124
Log reciprocal line intensity	0.09	0.39	0.00	0.96	0.74	0.66
Relative abundance $\text{Sn}^{120} = 100$	79.43	40.74	100.00	10.96	18.62	22.91
Percentage abundance	21.48	11.02	27.04	2.96	5.03	6.19

These figures give for tin a high isotopic moment 1.77. The mean mass number is 118.82. The packing fraction of Sn^{120} has been determined* and is -7.3 . Subtracting 0.09 on account of this and a further 0.01 for change of scale we get

$$\text{Atomic weight of tin} = 118.72 \pm 0.03.$$

A value in satisfactory agreement with 118.70 obtained by chemical methods.

Experiments with Chromium.

The first effective investigation of this element was made in 1923 by the method of accelerated anode rays.† The results were feeble but showed one distinct line at 52. As this agreed with the chemical atomic weight it was assumed that chromium was a simple element. The application of the more powerful and convenient method of the ordinary discharge tube has now been made possible through the preparation, by Dr. A. v. Grosse, of Berlin, of a suitable volatile compound, the hexacarbonyl. The vapour pressure of this white crystalline solid is appreciable at ordinary temperature but not high enough to give a sufficient flow through the customary fine glass "leak." The latter was therefore not used but instead the vapour was allowed to diffuse directly into the discharge bulb with no more obstruction than two stopcocks and a few centimetres of narrow bore tubing. Even with this arrangement the

* 'Proc. Roy. Soc.,' A, vol. 115, p. 506 (1927).

† 'Phil. Mag.,' vol. 47, p. 397 (1924).

rate of diffusion was so low that no difficulty was experienced in keeping the pressure down by slow pumping.

The beams of rays obtained were vastly more intense than those given by the anode rays and it was soon realised that chromium had four isotopes, 50, 52, 53, 54, of which 52 was much the strongest. Of these the lightest is isobaric with the doubtful Ti^{50} and the heaviest with Fe^{54} . It was impossible to hold the discharge constant for any considerable length of time and the relative abundance was determined by the method of intermittent exposures. In order to find the ratio between 52 and the next most abundant 53, the rotating contact maker was set at 40° giving a ratio of 8 to 1. Under these conditions the reduced intensity of 52 was equal to that of 53 within experimental error. To determine the ratios of the three weaker isotopes a 2 to 1 ratio was used and the values obtained by interpolation on a curve.

Packing Fraction of Chromium.—A provisional value for this constant was obtained by comparing its 52 line with CO_2 44. The only near ratio available for this was $\text{C} : \text{CH}_2$. The latter line was introduced by allowing a trace of methane to flow into the discharge tube with the vapour of the carbonyl, but its exact mass is doubtful owing to the presence of Si^{28++} and possibly CO^{++} and N. In addition the two ratios have too large a numerical difference for really accurate measurement. From the data obtained the most probable value of the packing fraction appears to be -10 with a maximum possible uncertainty of ± 3 . This is in good agreement with the curve.

Chromium Results.

Mass numbers of isotopes	50	52	53	54
Log reciprocal line intensity	1.20	0.00	0.903	1.44
Relative abundance $\text{Cr}^{52} = 100$	0.03	100.00	12.83	3.80
Percentage abundance	4.9	81.6	10.4	3.1

The concentration of the weight in one isotope gives chromium the very low isotopic moment 0.31 and at the same time enables the mean mass number to be fixed with unusual accuracy at 52.068. This corrected for packing fraction and change of scale give

$$\text{Atomic weight of chromium} = 52.011 \pm 0.006.$$

A value virtually identical with the chemical one.

Experiments with Molybdenum.

The first attempts to obtain the mass-spectrum of the element were made by the method of accelerated anode rays. These were entirely unsuccessful* and the chance of obtaining a suitable volatile compound seemed remote until a specimen of the carbonyl probably $\text{Mo}(\text{CO})_6$, was prepared by Dr. A. v. Grosse. This is very like the chromium compound in volatility and other physical properties and was found to work almost as satisfactorily when admitted to the discharge bulb in exactly the same way.

The chemical atomic weight of molybdenum is practically a whole number, and Russell, by a theory markedly successful in many cases and founded on analogies from the known radioactive disintegrations, had confidently predicted it to be a simple element of mass number 96.† It was therefore somewhat surprising to find that its mass-spectrum contained no less than seven lines 92, 94, 95, 96, 97, 98, 100, three of which form isobaric pairs with Zr^{92} , Zr^{94} and the doubtful Zr^{96} . This group shows a similarity of abundance more striking than that of any other element of such complexity.

The total intensity of the group of molybdenum rays was probably less than that yielded by chromium and as this is divided among seven almost equal lines it was by no means easy to get lines dark enough for good photometry even with the maximum practicable exposures. For this reason the group had to be photographed at a position on the plate giving less than the normal resolution. Under these conditions it was only just possible to use the method of intermittent exposures. The small range of intensity rendered a single ratio of two to one sufficient for the measurements, but the extreme closeness of the lines impairs the accuracy of the photometry so that the ratio must be taken as less certain than usual.

A further difficulty was the inevitable presence of the doubly charged mercury group. The very weak line Hg^{198}_{++} could be virtually eliminated, but even with the utmost precautions it was not possible to reduce Hg^{200}_{++} below a considerable fraction of the practically coincident line Mo^{100} . In order to arrive at the true line intensity of the latter the lines of the mercury group had to be photometered up and the effect of the mercury line, estimated from the known ratios of intensity of the mercury group, subtracted. Incidentally these measurements showed that no molybdenum lines of appreciable strength

* 'Phil. Mag.,' vol. 47, p. 399 (1924).

† 'Nature,' vol. 112, p. 588 (1923).

could be present at 99 or 101. On account of these difficulties no great accuracy can be claimed for the abundance ratios obtained.

Packing Fraction of Molybdenum.—A provisional value for the packing fractions of Mo^{98} and Mo^{100} was obtained by estimating the position of these lines among those of mercury, which were all assumed to have a packing fraction of 0.8. This was done by photometer curves and the most probable value appears the same for both lines and equal to -5.5 . This is only a rough value but adequate for calculating the atomic weight. It is a definitely smaller negative value than that expected from the packing fraction curve.

Molybdenum Results.

Mass numbers of isotopes	92	94	95	96	97	98	100
Log reciprocal line intensity	0.17	0.34	0.15	0.10	0.38	0.00	0.38
Relative abundance $\text{Mo}^{98} = 100$	61.6	43.6	67.6	77.6	41.7	100.00	42.7
Percentage abundance	14.2	10.0	15.5	17.8	9.6	23.0	9.8

These results, which must be taken as provisional only, give for molybdenum an isotopic moment of 1.87, the highest yet measured, and a mean mass number of 96.02₅. Correcting for packing fraction and change of scale we get

$$\text{Atomic weight of molybdenum} = 95.97 \pm 0.06.$$

A satisfactory confirmation of the value 96.0 now in use.

Relations between Abundance Ratios.

In all seven of the most complex elements of even atomic number have now been quantitatively investigated. An element of n isotopes provides $\frac{1}{2}n(n-1)$ ratios of abundance so that no less than 175 of these numbers are available. It must be admitted, however, that analyses of these show so far no obvious groupings or relationships, and are to this extent disappointing. The research is being continued and the results on other complex elements will be published in due course.

Amended Table of Isotopes.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Mass numbers of isotopes in order of abundance.
Cr	24	52.01	4	52, 53, 50, 54.
Zn	30	65.38	7	64, 66, 68, 67, 65, 69, 70.
Mo	42	96.0	7	98, 96, 95, 92, 94, 97, 100.
Sn	50	118.70	11	120, 118, 116, 119, 117, 124, 122, 121, 112, 114, 115.

In conclusion the author wishes to express his thanks to Mr. M. B. Dewey for the preparation of the cadmium methyl and to Dr. A. v. Grosse who provided the specimens of chromium and molybdenum carbonyls which gave such successful results.

Summary.

Further experiments on the measurement of the relative abundance of isotopes by means of the photometrical intensity of lines in mass-spectra are described, unsuccessful with cadmium and germanium, successful with zinc, tin, chromium and molybdenum.

These have resulted in correction of the order of intensity in the case of zinc and tin and in the discovery of three new isotopes of chromium and the seven isotopes of molybdenum.

Numerical values of considerable accuracy are given for the percentage abundance of each isotope and for packing fractions where not known already. From these the isotopic moments and atomic weights of each element are calculated. The latter are all in good agreement with the chemical values.

The Rate of Loss of Energy by β -Particles in Passing through Matter.

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§ 1. *Introduction.*

This paper deals with the rate of loss of energy by β -particles in passing through matter. Though much work has been done on this effect,* beginning with the experiments of Lenard in 1895, there is still a great deal of uncertainty

* W. Wilson, 'Proc. Roy. Soc.,' A, vol. 82, p. 612 (1909), vol. 84, p. 141 (1910), and vol. 87, p. 310 (1912); R. Whiddington, 'Proc. Roy. Soc.,' A, vol. 86, p. 300 (1911) and vol. 89, p. 554 (1913); von Baeyer, 'Phys. Z.,' vol. 23, p. 485 (1912); Danyasz, 'C. R.,' vol. 154, p. 1502 (1912); 'J. Physique,' vol. 3, p. 949 (1913) and vol. 5, p. 527 (1915); W. F. Rawlinson, 'Phil. Mag.,' vol. 30, p. 627 (1915); Varder, 'Phil. Mag.,' vol. 29, p. 725 (1915); J. A. Gray and A. V. Douglas, 'Phys. Rev.,' vol. 19, p. 432 (1922); Douglas, 'Trans. Roy. Soc.,' Canada, vol. 16, p. 113 (1922); B. F. J. Schonland, 'Proc. Roy. Soc.,' A, vol. 104, p. 235 (1923) and vol. 108, p. 187 (1925); Terrill, 'Phys. Rev.,' vol. 22, p. 101 (1923), and vol. 24, p. 616 (1924); J. Thibaud, 'J. Physique,' vol. 6, p. 334 (1925); J. d'Espine, 'C. R.,' vol. 182, p. 458 (1926); 'J. Physique,' vol. 8, p. 502 (1927); E. Madgwick, 'Camb. Phil. Soc. Proc.,' vol. 120, p. 701 (1928); E. Becker, 'Ann. Physik,' vol. 78, p. 209 (1925); P. White and G. Millington, 'Proc. Roy. Soc.,' A, vol. 120, p. 701 (1928).

in connection with it. This is largely due to the fact that in most of the experiments which have been carried out the observations cannot be accurately interpreted on account of the complications which arise from the considerable scattering and straggling which β -particles suffer in traversing matter. There are, however, at the present time two methods of obtaining values for the rate of loss of energy by β -particles which are practically free from these sources of error. One is the Wilson cloud method, and the other consists of an analysis of the losses of energy suffered by β -particles in traversing *thin* material foils—of thicknesses small compared with the range of the particles. The purpose of the present paper is to give reliable experimental values for the rate of loss of energy by β -particles obtained by means of these methods. Those for “slow” β -particles with velocities between about 0.1 and 0.3 times the velocity of light (*c*) are the results of new observations by the cloud method on the ranges of β -particles in oxygen, and of previous observations, using the same method, by Nuttall and the author* on the ranges in hydrogen and in argon. The ranges obtained by the cloud method differ considerably from those obtained in experiments in which the effect of intercepting a beam of β -particles with a foil on the number, or energy, of the emergent particles is observed.† The quantity taken as the “range” in some of these experiments can also be measured by the cloud method. Measurements of this kind have been made, and they show that the difference between the range obtained by the cloud method and that obtained by the “foil” method is entirely due to the errors incurred in the latter by the effects of scattering and straggling. The cloud method is not suitable for determining the ranges of “fast” β -particles, since the track of a β -particle with an initial velocity of about 0.5 *c*. or greater is too long to be contained in a cloud chamber of reasonable dimensions.‡ The values which are given in this paper for the rate of loss of energy by fast β -particles are based on observations made by means of the second method mentioned above, in which the β -particles are passed through thin foils. The effects of scattering and straggling in such experiments were recently calculated by the writer.§ The results obtained in that work enable

* ‘Phil. Mag.,’ vol. 2, p. 1109 (1926).

† Wilson, Varder, Gray and Douglas, Schonland, Terrill and Madgwick, *loc. cit.*

‡ Throughout the paper the term “slow” β -particles is used to denote electrons with velocities between about 0.1 *c*. and 0.4 *c*. (energy between 2,000 and 50,000 volts), whilst electrons with velocity greater than about 0.5 *c*. (energy greater than about 100,000 volts) are referred to as “fast” β -particles.

§ ‘Proc. Roy. Soc.,’ A, vol. 125, p. 420 (1929).

us to make an accurate interpretation of the observations, provided the thickness of the foil used in the experiments is not greater than about a fifth of the range of the β -particles.* The only experiments in which this condition is satisfied, and in which the data obtained are sufficiently full, are those carried out by White and Millington,† and the results given here for fast β -particles are based on an analysis of the observations of these workers. The results refer to a range of velocity from about 0.5 c. to 0.97 c. These and the results for "slow" β -particles cover a range of velocity from about 0.1 c. to 0.97 c.—from a region where relatively effects are small to where they are large. It might be pointed out that this range is much wider than that which is open to investigation in the case of α -particles. It also refers to greater velocities‡ and this circumstance is of considerable importance in connection with the conditions of applicability of the theoretical formulæ.

The theory of the loss of energy by moving electric particles according to classical mechanics was considered by Bohr in 1913, and the formula obtained by him also very nearly represents the requirements of the new quantum theory as far as these have been ascertained.§ In this paper we shall compare the experimental results with Bohr's formulæ. A fuller discussion of the relation between theory and experiment is given in the next paper, which deals with the collective significance of the present results, and of the results of previous investigations by the writer on other phenomena connected with the loss of energy by β -particles.

The theoretical formulæ required in this paper are given in § 2. The experimental results obtained for "slow" β -particles by the cloud method are given in § 3, and compared with the theoretical values. In this section an account is also given of the observations made by the cloud method on the quantity taken as the range in "foil" experiments. The results obtained for fast β -particles are given in § 4.

§ 2. Theoretical Formulæ.

According to Bohr's theory, the average rate of loss of energy by β -particles with velocities small compared with that of light is given by

$$\overline{dT}/dx = (4\pi Ne^4/mv^2) \sum_{r=1}^{r=\infty} \log(\gamma v^3/4\pi v_r e^2), \quad (1)$$

* The effect of scattering depends, of course, on the atomic number of the element traversed, and this result applies to light elements such as aluminium.

† *Loc. cit.*

‡ The velocity of the fastest α -particles available is only about 0.07 c.

§ J. A. Gaunt, 'Camb. Phil. Soc. Proc.,' vol. 33, p. 732 (1927).

where $\overline{dT}$ is the average energy lost in travelling a distance dx , N is the number of atoms of the element traversed per unit volume, Z is the number of electrons per atom, ν_r is the natural frequency of the r th electron in the atom, e and m are the electronic charge and mass respectively, v is the velocity of the β -particle, and γ is a constant the numerical value of which is 1.123. If we represent the geometric mean of the frequencies of the electrons in the atom by $\bar{\nu}$ and substitute for γ , then (1) may be written

$$\overline{dT}/dx = (4\pi NZe^4/mv^2) \log (1.123 v^3/4\pi\bar{\nu}e^2). \quad (1A)$$

Bohr's formula requires a small correction on account of the fact that in practice the electron with greater energy after a collision between a β -particle and an electron is taken as the β -particle.* This correction may be made by introducing a factor $\sqrt{\epsilon/4}$ into the log term, the corrected value being

$$\overline{dT}/dx = (4\pi NZe^4/mv^2) \log (0.92 v^3/4\pi\bar{\nu}e^2). \quad (2)$$

The correction amounts to only about 3 per cent. in $\overline{dT}/dx$.

The conditions of applicability of Bohr's formulæ require

$$2e^2/mv^2 \ll \rho \ll v/v. \quad (3)$$

The first quantity is the distance the "knocked" electron would move during a collision if it were free, whilst v/v represents the distance the β -particle travels during one free period of the atomic electron. ρ represents the dimensions of the orbit of the atomic electron.

As we shall see in § 4, the experimental results for fast β -particles obtained with the "foil" method do not refer to the rate of loss of energy due to *all* collisions, but only to collisions in which the energy lost is less than a certain quantity M . The theoretical value of this quantity, corrected for relativity effects, is according to Bohr's theory given by

$$d_M T/dx = (2\pi NZe^4/mv^2) \{ \log M - \log (8\pi^2 e^4 \bar{\nu}^2 / 1.123^2 mc^4) + \log (\beta^4 / 1 - \beta^2) - \beta^2 \}, \quad (4)$$

where β represents the ratio of the velocity of the β -particle to that of light.

The conditions of applicability of this formula require, in addition to (3),

$$(8\pi^2 e^4 / 1.123^2 m) v^2/v^4 \ll M \ll T. \quad (5)$$

On the quantum theory, as applied by Gaunt,

$$M \gg J \quad (5A)$$

* A head-on collision, for instance, contributes nothing to the observed stopping power, though the original β -particle loses all its energy in such a collision.

where J is the ionisation potential, must also be satisfied (see following paper).

In comparing theory and experiment it is often more convenient to deal with the quantity

$$P = (dT/dx) \div (2\pi NZe^4/mv^2), \quad (6)$$

than with dT/dx itself. For a given velocity P is a measure of the average stopping power per electron of the material traversed. Its values corresponding to (2) and (4) are

$$P = 2 \log (0.92 v^3/4\pi\bar{v}e^2) \quad (7)$$

$$P_M = \log M - \log (8\pi^2 e^4 \bar{v}^2/1.123^2 mc^4) + \log (\beta^4/1 - \beta^2) - \beta^2 \quad (8)$$

respectively.

In dealing with the experimental results we shall also have occasion to refer to the classical number of collisions $\phi_0(Q) dQ$ in which a β -particle loses energy between Q and $Q + dQ$ in traversing an atmosphere of free electrons initially at rest. This is given by

$$\phi_0(Q) = (2\pi e^4 n/mv^2)/Q^2 \quad (9)$$

where n is the number of electrons per unit volume.

§ 3. *Ranges of, and Rate of Loss of Energy by, "Slow" β -particles,*

$$(0.1 < \beta < 0.3).$$

The theoretical formulæ for the rate of loss of energy given in the preceding section refer to the energy lost by a β -particle in travelling a given distance measured *along the path* of the particle. On account of scattering, this distance may differ considerably from the direct distance between two points on its path. The formulæ also deal with the *average* rate of loss of energy. In view of these facts, the quantity that it is desirable to determine in experiments on the ranges is the average value, $\bar{R}$, of the ranges measured along the paths of the particles. The cloud method enables us to determine this quantity, and it is the method used in the present observations. It was previously used for measuring ranges by Wilson* in 1922 and later by Nuttall and the author.† As in the experiments of the latter, the present observations were made on the ranges of β -particles generated photoelectrically in a Wilson cloud chamber by X-rays reflected from a crystal, the initial energy being accurately known from the wave-length of the X-rays.‡

* 'Proc. Roy. Soc.,' A, vol. 104, pp. 1 and 192 (1923).

† *Loc. cit.*

‡ Characteristic rays were reflected and the wave-length was known within about 0.2 per cent.

The ranges obtained in the present and previous investigations with the cloud method are in substantial agreement, but they all differ considerably from the ranges obtained in experiments in which the β -particles are passed through solid foils, such as those carried out by Schonland.* The ranges in aluminium according to the formula obtained by Nuttall and Williams for light elements are, for instance, about 40 per cent. greater than the ranges in aluminium obtained by Schonland with the foil method.† In view of the many investigations that have been made by the foil method, it is desirable that this large difference between the results obtained by means of it and those obtained by the cloud method be explained. For this purpose observations have been made by the cloud method on the quantity taken as the range in Schonland's experiments. In the latter the β -particles are passed through foils of different thicknesses and the number of emerging particles observed. Schonland plots this number against the thickness of the foil and takes the intercept on the thickness axis made by the tangent to the flat part of the curve as the range. The same quantity can be determined by the cloud method by measuring the distance R_f travelled by a β -particle parallel to its initial direction (see fig. 1). The number of β -particles for which R_f is greater than a certain quantity d is then the number that would emerge from a foil of thickness d . The results for β -particles with initial energy of 19,590 volts in oxygen are represented by curve (a) in fig. 2A, and for β -particles with the same initial energy in argon by the curve in fig. 2B.‡ The quantity taken as the range in Schonland's experiments is represented by R_F in these figures. For oxygen the true average range $\bar{R}$ is about 24 per cent. greater than R_F , and for argon $\bar{R}$ is

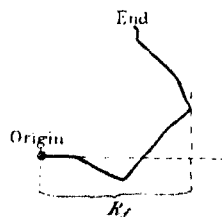


FIG. 1.

* *Loc. cit.*

† According to the formula of Nuttall and Williams, the mean range R of β -particles with initial energy T electron-volts, in matter containing n electrons per cubic centimetre, is given by

$$\bar{R} = 7.7 \times 10^{11} T^2/n, \quad (10)$$

this result applying to elements with atomic number up to argon ($z = 18$). The difference between the range in aluminium according to this formula and that obtained by Schonland cannot be attributed to the fact that (10) is based on observations on gases; since both on theoretical grounds and from the observed ranges of α -particles in gases and solids, there is no reason to expect any appreciable effect of physical state on the stopping power of a substance per atom.

‡ The individual values of R_f in these cases were not measured with a high degree of accuracy. The resultant curve is, however, sufficiently accurate for our present purpose.

about 48 per cent. greater than R_F . The ratio of $\bar{R}$ to R_F depends upon the ratio of the scattering power of the material traversed to its stopping power, and is therefore greater the greater the atomic number. The atomic number of aluminium is midway between those of oxygen and argon, so that the ratio of R to R_F for aluminium is in the neighbourhood of 1.35. This agrees satisfactorily with the ratio of the range in aluminium given by the formula of Nuttall and Williams, to the range obtained by Schonland.* The observations

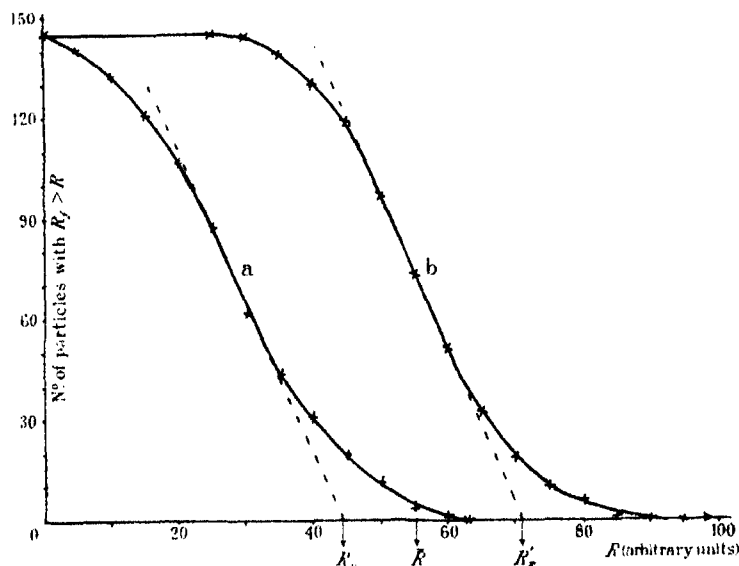


FIG. 2A.—Oxygen. True Mean Range, $\bar{R} = 55.1$. Foil Range, $R_F = 44$. Foil Range (no scattering) $R'_F = 71$.

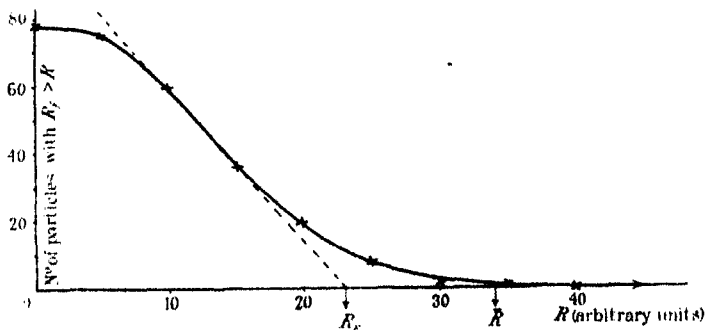


FIG. 2B.—Argon. True Mean Range, $\bar{R} = 34$. Foil Range, $R_F = 23$.

* In the case of β -particles with initial energy of 24,300 volts, for instance, the ratio of the range according to (10) to the range obtained by Schonland is 1.37.

represented in figs. 2A and 2B thus reproduce the results obtained by the foil method, and since we know that the difference between $\bar{R}$ and R_F in the present experiments is entirely due to scattering and straggling, it follows that these are the effects which are the sources of error in the foil method. Before leaving this matter it is instructive to consider curve (b) in fig. 2A. It represents the results that would be obtained by the foil method if *no scattering* took place, and has been constructed by taking R_F equal to the true range measured along the path of the particle. The value of the ratio $\bar{R}/R_F$ for this curve is 0.78. This result shows that if no scattering took place the range obtained by the foil method would on account of straggling be nearly 30 per cent. *greater* than the average range. Thus straggling as well as scattering has considerable effect on the range obtained in foil experiments, the effect of straggling opposing that of scattering. It is the fact that both these effects are involved, and that they are both of a first order of magnitude that makes it practically impossible to make an accurate interpretation of the observations made on ranges by the foil method.

The observations of Nuttall and Williams on the ranges were made on β -particles of different initial energies in different gases, about 12 different cases being dealt with. The results show the nature of the variation of range with initial energy and atomic number of the element traversed, but, as only about 20 "tracks" were measured in each case, the absolute value of the range was in no case found with great accuracy. The purpose of the present observations on ranges is to supplement these results by obtaining the absolute value of the stopping-power for one or two cases as accurately as possible. β -particles show considerable straggling, the curve of distribution of ranges having a half-maximum width equal to about 40 to 50 per cent. of the mean range. As a result, it is necessary to make observations on a large number of β -particles in order to obtain an accurate value of the mean range. In the present work observations were made on about 400 β -particles, the probable error due to straggling in the two cases investigated being not more than 1 or 2 per cent. In these observations special attention was also paid to tracks with "branches." These have much less than the average range and are mostly responsible for the "tail" of the straggling curve on the short-range side. They do not occur very frequently, but if they are not included in the observations the corresponding mean range does not give the rate of loss of energy due to *all* collisions. In the present observations the total number of tracks measured is sufficiently large that those with branches are well represented, so that the results give the rate of loss of energy due to all collisions.

A third matter which must be considered in order to obtain accurate results is that even with the cloud method it is not possible to follow the path of a particle right up to the end of its range owing to the effects of scattering and of the finite thickness of the photograph of cloud tracks. The error which thus arises from scattering can, however, be allowed for. The correction is small, and we shall therefore only briefly mention the following points upon which it is based :—(1) Under the same conditions of observation the correction is the same for β -particles with different initial energies, being an “end” correction; (2) the direct range from the origin of a track to its end can be measured without any errors due to scattering; (3) the ratio, r , of the range, measured along the path to the direct range, is for the same gas practically independent of the initial energy, T ; whilst the small variation with T that does take place can be estimated from observations on the much larger variations of r with atomic number. The estimated magnitude of the correction in the present experiments is only 0.008 cm. (at N.T.P.), which is about 1 per cent. of the ranges of the faster group of β -particles dealt with, and about 7 per cent. of the ranges of the slower group. The correction is of course added to the range.

The observations were made on the ranges in oxygen of 209 β -particles with initial energy of 19,590 volts, of 87 with initial energy of 22,130 volts, and of 114 with initial energy of 7,560 volts. The mean ranges obtained for these three groups (reduced to N.T.P. conditions) are 0.644 cm., 0.847 cm., and 0.117 cm. respectively. The initial energies of the first two groups are so close that it is better to consider them together and express the results as the range for an intermediate energy.* By combining the two groups in this way, we obtain a range of 0.709 cm. for β -particles, with initial energy of 20,440 volts. This result depends on observations on about 300 tracks, and the probable error due to straggling is only 1 per cent.

Before giving the table of results, it is necessary to point out that, owing to the existence of straggling, the mean rate of loss of energy, represented by $\overline{dT}/dx$, is not exactly equal to the differential $dT/d\overline{R}$, where $\overline{R}$ is the mean range of particles with initial energy T .† This has been allowed for in the present

* As the range of β -particles does not vary linearly with their initial energy, the arithmetic mean range of two groups of β -particles is not exactly equal to the range of β -particles possessing their mean energy. The energies of the two groups under consideration are, however, so close that this effect is negligible, being less than 0.1 per cent.

† Let $\overline{dT}$ be the average energy lost by β -particles in travelling a distance dx . Owing to straggling, the actual energy losses suffered by individual particles differ from $\overline{dT}$, and unless the mean range is a linear function of the energy, the mean remaining range of

work by using the following relation between $\overline{dT}/dx$ and $dT/d\overline{R}$, derived by the writer* some time ago

$$\begin{aligned} \overline{dT}/dx - dT/d\overline{R} = & \frac{1}{2!} \frac{d^2\overline{R}}{dT^2} \frac{dT}{d\overline{R}} \int_{Q_i}^{Q_m} Q^2 \phi(Q) dQ + \dots \\ & + (-1)^{r+1} \frac{1}{r!} \frac{d^r\overline{R}}{dT^r} \frac{dT}{d\overline{R}} \int_{Q_i}^{Q_m} Q^r \phi(Q) dQ + \dots \quad (11) \end{aligned}$$

$\phi(Q) dQ$ represents the frequency of collisions in which the energy lost is between Q and $Q + dQ$, and Q_i and Q_m are the limits to the possible value of Q . The right-hand side of this equation is almost entirely represented by the first term, whilst the integral in this term depends almost entirely on the values of $\phi(Q)$ for large values of Q . This integral can therefore, if necessary, be evaluated experimentally from observations with the cloud method on the frequency of branches.† This means that we can deduce the actual values of $\overline{dT}/dx$ from the experimental values of $dT/d\overline{R}$ without recourse to theory. However, as the difference between $\overline{dT}/dx$ and $dT/d\overline{R}$ is only about 2 per cent., and as the observed number of branches is roughly the same as the theoretical value, whether we evaluate the right-hand side of (11) experimentally or not, is more a matter of principle than of numerical importance.

The experimental results and the corresponding theoretical values according to Bohr's formulæ are given in the following tables. The experimental values for oxygen are those obtained in the present observations, the most accurate result of all being that for the distance travelled in losing energy from 20,440 volts to 7,560 volts.‡ The results for argon and hydrogen are those obtained in the observations of Nuttall and Williams with a small correction for the effect of branches. In Table I the results are expressed in terms of ranges, and in Table II in terms of the quantity P defined by (6).

In calculating the theoretical values given in the above tables Stoner's distributions of electrons in the atoms are assumed, and the natural frequencies, ν , of the electrons (which appear in Bohr's formula) are taken equal to the ionisation potential, J , divided by Planck's constant, *i.e.*,

$$\nu = J/h. \quad (12)$$

all the particles is not the same as the mean range of particles, all of which possess the mean remaining energy $T - \overline{dT}$. The mean remaining range, therefore, depends not only upon the mean loss of energy in travelling the distance dx , but also upon the straggling produced in this distance.

* 'Camb. Phil. Soc. Proc.', vol. 24, p. 315 (1928).

† E. J. Williams, 'Proc. Roy. Soc., A, vol. 128, p. 459 (1930).

‡ This is independent of any "end" correction.

Table I.—Ranges of β -particles.

Gas.	Initial energy, T (volts).	Initial velocity (in terms of c).	Observed Range, R, at N.T.P. (cm.).	Theoretical range according to Bohr's formula (equation (2) for $\overline{dT}/dx$.)	Observed range + theoretical range.
Oxygen	7,560	0.170	0.11,	0.070	1.67
	20,440	0.275	0.70,	0.417	1.70
	20,440-7,560	0.275-0.170	0.59,	0.347	1.70
Hydrogen	4,800	0.136	0.35	0.214	1.64
	7,560	0.170	0.72	0.492	1.47
Argon.....	20,440	0.275	0.67	0.410	1.64

Table II.—Stopping Power per Electron, $P = \overline{dT}/dx \div (2\pi NZe^4/mv^3)$.

Gas.	Energy (volts).	Velocity, (in terms of c).	P (observed).	P (theoretical) (equation (7)).
Oxygen	4,800	0.136	8.9	14.8
	14,000	0.230	10.6	18.0
Hydrogen	3,100	0.110	9.9	15.8
	4,800	0.136	11.7	17.1
Argon	14,000	0.230	10.0	16.3

The observed values of J are used in calculating v from this formula.* As v occurs inside a log term, the expression for the stopping power is not very sensitive to changes in its value. A change of 50 per cent. in v , for instance, affects the stopping power by only 4 per cent. It is therefore not important to know the exact value of v .

Numerous comparisons of Bohr's formula with experiment have been made by other workers, but in no case is there an indication of the large discrepancies found here. In his original paper on the subject, Bohr showed that the varia-

* The following are the atomic data used :—

Hydrogen, H_1 .	Oxygen, O_2 .	Argon, A_1 .
2 electrons, $J = 16$ volts.	4K electrons, $J = 500$.	2K electrons, $J = 3200$.
	4L „ $J = 50$.	2L „ $J = 320$.
	8L „ $J = 14$.	6L „ $J = 240$.
		8M „ $J = 15$.

tion with velocity of the stopping power of air for α -particles was satisfactorily given by his formula, and that the values of the frequency ν which had to be substituted in the formula to give the absolute value of the observed stopping power, were in reasonable accord with the current theory of the atom. Fowler* in 1925 (in a reconsideration of Bohr's theory on the basis of electron orbits), considered the relation of Bohr's formula to the results for α -particles traversing hydrogen. He found that the theoretical value of the stopping power for the α -particles from RaC ($V \approx 2 \times 10^9$ cm. sec.) was within about 5 per cent. of the theoretical value. The case of fast β -particles was considered by White and Millington,† who found that the theoretical and observed values did not differ appreciably, though the differences were outside experimental error. The validity of the formula for slow β -particles traversing aluminium was considered by Schonland‡ and he concluded that the theoretical stopping power for the whole range of velocity investigated was in "excellent agreement" with experiment. Previous comparisons with experiment are therefore in favour of Bohr's formula as a quantitative representation of the experimental results.

The results given in the above tables do not support this position. The observed values of the ranges are on the average about 60 per cent. greater than the theoretical values.§ The conditions of applicability of Bohr's formula, given by (3), are fully satisfied in all the cases represented in the tables, so that the differences cannot be attributed to this source. Neither can they be attributed to uncertainties in the data used for calculating the theoretical values. The frequency ν is the only quantity to which such uncertainty can be attached, but the theoretical values are so insensitive to ν that its order of magnitude would have to be altered in order to explain the observations. Moreover, the differences between theory and experiment are nearly as large for hydrogen as for the other gases, though there is much less doubt about the data for hydrogen, there being only one energy level for which the dispersion frequency is accurately known.

The values according to Bohr's formula have also been calculated using values of ν which make the formula fit with the observed values of the stopping power of the elements concerned for α -particles. Even with ν adjusted in this

* 'Camb. Phil. Soc. Proc.,' vol. 22 (1925).

† *Loc. cit.*

‡ *Loc. cit.*

§ This large discrepancy was first demonstrated by the writer in 'Manch. Mem.,' vol. 71, p. 25 (1927), in discussing the cloud observations made in collaboration with J. M. Nuttall.

way the discrepancies are almost as large, the observed ranges being still about 40 per cent. greater than the theoretical ranges.* This result also indicates that the variation of the rate of loss of energy from α -particles to β -particles, i.e., with the charge and mass of the moving particle, is not correctly given by Bohr's formula.

As regards the variation with velocity, we see that both the observed and theoretical values of P , in Table II, increase with the velocity. Since P is defined as $(\overline{dT}/dx) \times k'v^2$, this means a departure from the Thomson-Whiddington fourth-power law of the variation of range with velocity. The most accurate values given in the above tables are those of the present observations on oxygen. These correspond to the law

$$\overline{R} \propto v^{3.75} \propto T^{1.85}. \quad (13)^\dagger$$

The departure from the fourth-power law is definitely outside experimental error. The observed departure, in terms of the increase in P with velocity, is, however, not as large as that required by Bohr's formula.

Bohr's formula also very nearly represents the requirements of the new quantum theory as far as they have been ascertained by Gaunt.‡ Gaunt's calculations were actually made for hydrogen atoms, but it is very unlikely that the difference between Bohr's formula and experiment can on the quantum theory be attributed to this fact. In the first place, if this were the case, we would expect the difference between Bohr's formula and experiment to be less the closer the approach of the atoms dealt with to hydrogen atoms. The atoms in the hydrogen molecule are a good and probably the closest approach to hydrogen atoms available, but we see from the above tables that the difference between the theoretical values and the observed values is almost as big for H_2 as for the other gases dealt with. The actual value of the observed stopping power of H_2 corresponds to a value of the constant γ in the theoretical formula (see equation (1)), which is about 20 times less than the theoretical value of γ calculated by Gaunt for hydrogen atoms. Though a small variation of γ from H to H_2 may be allowed on theoretical grounds, it is difficult to

* In making a similar comparison for aluminium, Schonland (*loc. cit.*) found that the theoretical values agreed within 1 or 2 per cent. with the observed values. As shown at the beginning of this section, the ranges obtained by the method used by Schonland involve large errors due to scattering and straggling, and the agreement of the results with theory is accidental.

† The index of T is not exactly one-half that of v on account of relativity effects.

‡ *Loc. cit.*

admit a variation of this magnitude.* Another objection to attributing the difference between the theoretical and observed values in the above tables to the fact that Gaunt's calculations were made for hydrogen atoms is that Bohr's formula fails to give correctly the variation of the stopping power from α -particles to β -particles. This shows that the exact *form* of Bohr's formula is not correct, whilst Gaunt points out that if calculations similar to those made by him for hydrogen atoms were made for H_2 or other gases, the form of Bohr's formula would certainly be maintained. We conclude that though Gaunt's calculations were made for hydrogen atoms, the discrepancies between the theoretical formulæ and experiment cannot be attributed to this fact.

§ 4. *Rate of Loss of Energy by Fast β -particles.*

As mentioned in the introduction, the values of the stopping power for fast β -particles given in this paper are based on experiments on the losses of energy suffered by β -particles in passing through thin foils. In such experiments the energy of the emergent particles is observed by a magnetic analysis—usually in conjunction with a photographic method. The spectrum of the β -particles not intercepted by the foil consists of a narrow line, whilst those which have traversed it give a wider line in a different position. The distance from the first line to the point of maximum intensity in the second is called the peak-displacement. This is the quantity measured in the experiments, and it represents the most probable loss of energy, $d_p T$, in traversing the foil.

The statistical theory of the energy losses in thin foils was first considered by Bohr† and later more fully by the writer.‡ The calculations made show that $d_p T$ is very much less than the average loss of energy, on account of a small number of violent collisions which little affect the shape of the curve of distribution of losses in the neighbourhood of its maximum, but which contribute appreciably to the average loss. Bohr made an approximate estimate of $d_p T$, and showed that it was little affected by the collisions for which Q is greater than a certain quantity, S , which, using the classical expression (9) for $\phi(Q)$ is equal to $(2\pi NZe^4/mv^2)t = kt$, t being the thickness of the foil. In the more detailed calculations made by the writer the actual form of the curve

* The difference between the observed and theoretical stopping power of hydrogen for α -particles is much less than for β -particles, and results for α -particles therefore give a false impression of the degree of accuracy of Gaunt's formula—the value of γ corresponding to the observed stopping power of molecular hydrogen for α -particles being of the same order of magnitude as its value in Gaunt's formula for atomic hydrogen.

† 'Phil. Mag.,' vol. 30, p. 581 (1915).

‡ 'Proc. Roy Soc.,' A, vol. 125, p. 420 (1929).

of distribution of losses is deduced, the position of the maximum, which gives $d_p T$, being thus accurately determined. According to the result obtained, the effective upper limit to the values of Q in the collisions which contribute to $d_p T$ is $1.2kt$. This result depends on the use of the classical value of $\phi(Q)$. The experimental results which we shall use here are those obtained in the experiments of White and Millington. The analysis of the *straggling* observed in these experiments shows that the actual values of $\phi(Q)$ in the neighbourhood of $Q = S$ are 2.3 times the classical values.* The actual upper limit to the values of Q which affect $d_p T$ in these experiments is therefore given by

$$S' = 2.3 \times 1.2 kt = 2.8 kt. \quad (14)$$

This differs appreciably from the classical limit, kt , used by Bohr, and, though the limit occurs in a log term, the error incurred in this respect by the use of Bohr's formula is about 10 per cent.

Since S' depends upon the thickness of the foil the most probable *rate* of loss of energy, $d_p T/dx$, also involves this quantity. The thickness of the foil used in the observations must therefore be given, as well as the values of $d_p T/dx$, in recording the experimental results. It is desirable that the experimental results be expressed independently of such an incidental factor as the thickness of the foil used in the experiments. In the present analysis this has been done by calculating from the observations on $d_p T/dx$ and t , the rate of loss of energy $d_w T/dx$ due to collisions for which Q is less than a constant value W . The relation between $d_w T/dx$ and $d_p T/dx$ is given by

$$d_w T/dx = d_p T/dx + 2.3 k \log (W/S'). \quad (15)^\dagger$$

In the experiment of White and Millington the values of S' vary from about 700 to 2000 volts, and in order that the reduction from $d_p T/dx$ to $d_w T/dx$ should involve as little change as possible, the value of W has been chosen equal to 1500 volts, which is within this range. With this value of W the reduction in no case exceeds 6 per cent.

The effect of scattering on the distribution of energy losses in the foil was considered in the writer's earlier paper on straggling. The results obtained in

* See p. 442 equation (26c) of earlier paper on straggling ('Proc. Roy. Soc.,' A, vol. 125, p. 420 (1929)).

† The actual value of $\phi(Q)$ in the region of $Q = S'$ is 2.3 times the classical value given by (9), i.e., equal to $2.3 k/Q^2$. The actual energy lost in collisions for which $S' < Q < W$ is therefore equal to $2.3 k \int_{S'}^W Q dQ/Q^3 = 2.3 k \log (W/S')$. This gives the difference between $d_w T/dx$ and $d_p T/dx$.

that work have been used in correcting the observed values of $d_w T/dx$ for this effect. A correction has also been made for the fact that the average velocity in the foil is not exactly equal to the incident velocity. This correction and that for scattering amount on the average to about 5 per cent.

The results are given in the following table. $d_w T$ is expressed in kilovolts and dx is expressed in terms of the "mass" traversed in mg./cm.². The experimental values are based on the observations of White and Millington, except for the first value ($\beta = 0.52$), which is deduced from an observation by Becker on the energy lost in passing through an aluminium foil.

Table III.—Rate of Loss of Energy in Mica by Fast β -particles due to Collisions for which $Q < 1,500$ Volts.

$v/C = \beta$.	T (kilo- volts).	Experimental values of $d_w T/dx$ (kilovolts per gm./cm. ²).	$d_w T/dx$ $\times \beta^{+1.4}$.	Theoretical values of $d_w T/dx$ (equation (16)).	Theoretical value + Experimen- tal value.	P_w (expt.) $\left[= \frac{d_w T}{dx} + \left(\frac{2\pi NZe^4}{mv^2} \right) \right]$.	P_w (Th.) (equa- tion(17)).
0.52	88	2600	1.06	5100	1.96	9.6	18.9
0.64	155	1980	1.02	3720	1.88	10.6	19.9
0.70	205	1680	1.07	3200	1.90	10.7	20.3
0.75	262	1600	1.05	2830	1.76	11.7	20.6
0.80	341	1440	1.11	2520	1.75	12.0	21.0
0.87	598	1360	1.02	2200	1.62	13.4	21.7
0.940	945	1110	1.07	1960	1.76	12.8	22.6
0.960	1310	1130	1.04	1910	1.69	13.6	23.0
0.990	3110	—	—	1920	—	—	24.4
0.9,0	1.3×10^4	—	—	2780	—	—	35.9

The theoretical value of $d_w T/dx$ is given by (4), provided we substitute W for M . The value thus obtained is

$$d_w T/dx = (2\pi NZe^4/mv^2) \{ \log W - \log (8\pi^2 e^4 v^2 / 1.123^2 mc^4) + \log (\beta^4 / 1 - \beta^2) - \beta^2 \} \quad (16)$$

the corresponding value of P is

$$P_w = \log W - \log (8\pi^2 e^4 v^2 / 1.123^2 mc^4) + \log (\beta^4 / 1 - \beta^2) - \beta^2 \quad (17)$$

The theoretical values given in the above table are calculated from these formulæ. These values are seen to be about 80 per cent. greater than the observed values.* This difference is greater than, though in the same direction

* The difference between Bohr's theory and experiment is much greater than that found by White and Millington in discussing their results. This is due to several causes, all of which act in the same direction. These include the statistical error in the formula for the peak-displacement used by White and Millington, the error due to scattering in the foil, and the fact that these authors did not consider the absolute theoretical values but only those calculated from values of v adjusted to fit α -particle data.

as that found for slow β -particles. The values of $d_w T/dx$ according to (16), using values of v which give the observed stopping power of mica for α -particles, have also been calculated. The values obtained, though nearer the experimental values, are still about 50 per cent. in excess of them.

The conditions of applicability of the above formulæ as far as the classical theory is concerned (equations (3) and (5)) require $Q_v \ll W (= 1500) \ll T$. These are fully satisfied. On the quantum theory it would, however, be more satisfactory if W were also appreciably greater than the ionisation potentials, J , of the electrons in the atoms traversed (equation (5A)). The material traversed in the experiments under consideration is mica, half the electrons in which have ionisation potentials under 100 volts. However, about 20 per cent. of the electrons in it are K electrons, for which J is about 500 volts and greater. The condition $W \gg J$ may therefore not be adequately satisfied. However, the values of $d_w T/dx$ for values of W greater than 1500 volts may be obtained by using experimental data for the values of $\phi(Q)$ for $Q > 1500$, obtained from an analysis of White and Millington's observations on straggling,* and from the observations of the author and Terroux† on the frequency of branches. It is found in this way that for $W = 10,000$ volts, the theoretical value of $d_w T/dx$ for β -particles of velocity $0.75 c$. is about 50 per cent. greater than the observed value, whilst with values of v adjusted to fit α -particle data, the excess is about 30 per cent. The discrepancies are less than for $W = 1500$, but as W is now much greater than the ionisation potential of the most firmly bound electrons in the material traversed, the discrepancies can no longer be possibly attributed to the condition $W \gg J$ not being satisfied.

We see from the table that the theoretical variation of P_w with velocity is approximately the same as the observed variation. In both cases P_w increases by about 4, as the velocity increases from $0.52 c$. to $0.96 c$.—half the theoretical variation being due to the relativity terms.

The constancy of the values in column 4 of the table shows that $d_w T/dx$ itself is within experimental error proportional to $\beta^{-1.4}$; its absolute value being approximately represented by

$$d_w T/dx = 1.06 \beta^{-1.4} \text{ kilovolts per gm./cm.}^2 \quad (18)$$

This law of variation with velocity is very nearly the same as that found for the variation of the primary ionisation by Williams and Terroux.‡ This important result is discussed in the following paper.

* *Loc. cit.*

† 'Proc. Roy. Soc.,' A, vol. 126, p. 289 (1930).

‡ *Loc. cit.*

§ 5. *Summary.*

Experimental values for the rate of loss of energy by β -particles with velocities ranging from 0.1 c. to 0.97 c. are given. The results for slow β -particles are based on observations made with the cloud method and those for fast β -particles ($0.5 < \beta < 0.97$) are obtained from an analysis of the observations of other workers on the energy lost by β -particles in passing through thin foils. In both cases the results are practically free from the effects of scattering and straggling—effects which considerably reduce the quantitative value of most of the experimental work which has been done on β -particles.

The relation of the results to the theoretical values required by the formulæ of Bohr and Gaunt is discussed. It is found that these formulæ differ from experiment by much more than is generally thought. The observed values of the rate of loss of energy for slow β -particles is about 50 per cent. greater than the theoretical values, whilst the loss of energy by fast β -particles, in collisions for which the energy lost is less than 1500 volts, is about 80 per cent. greater than the theoretical values. The discrepancies are almost as great if we assume values for the dispersion frequency ν of the atomic electrons, which make the theoretical formulæ agree with the observed stopping power of the substances concerned for α -particles. In emphasising these discrepancies it is not desired to overlook the general agreement which exists—the theoretical values being in all cases of the right order of magnitude and varying with the velocity in roughly the same way as the observed values.

*The Loss of Energy by β -Particles and its Distribution between
Different Kinds of Collisions.*

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To the writer's knowledge there is at present no appreciable evidence that the phenomena connected with the loss of energy by β -particles (and α -particles) in traversing matter, receive any better explanation from the quantum theory than they do from the classical theory. Indeed since previous discussions of the application of the quantum theory in this field are confined to the *average rate* of loss of energy they cannot possibly support or discredit the quantum theory any more than they do the classical theory, because as regards this effect the two theories have nearly the same requirements. The fundamental difference between the two theories is manifested not in the actual energy lost in travelling a given distance, but in the *distribution* of this loss of energy between different kinds of collisions. This distribution is intimately connected with such phenomena as primary ionisation, straggling and the production of "branches," and it is by dealing with these phenomena that we can test the characteristic features of the quantum theory. Investigations on these phenomena were recently made by the writer partly in collaboration with F. R. Terroux. In the accounts of their work given by these authors the relation of experiment to classical theory only is considered. Large discrepancies are found which are much bigger than the differences found in the preceding paper between the experimental values of the rate of loss of energy and the common requirements of the classical and quantum theories for this effect (represented approximately by Bohr's formula). In some cases such as the primary ionisation, the classical values are almost of a different order of magnitude from the experimental values. The question arises—is the fundamental departure which the quantum theory makes from the classical theory as regards the distribution of the energy lost, in the right direction to agree with experiment? The main purpose of the present paper is to investigate this matter. To do so it is first necessary to consider more closely than has hitherto been done the actual requirements of the quantum theory as regards the distribution of the loss of energy. In the quantum theory calculations made by Gaunt, this distribution is not explicitly dealt with, though its general features may readily be deduced from his work. Experimental data appropriate for the

present discussion are provided by the investigations referred to above. The comparison of theory and experiment which is made, though not resulting in unqualified support of the requirements of the quantum theory, gives striking proof that they depart from the classical requirements in the right direction. The actual differences between the requirements of the quantum theory, as far as they are ascertained, and the experimental results for the primary ionisation, straggling, and frequency of branches, are not greater than the difference between the observed rate of loss of energy and the common requirements of the classical and quantum theories for this phenomenon. This means of course that the discrepancies may still be appreciable, and though the quantum theory as far as it has been applied gives a general explanation of many results which are unintelligible on the classical theory, there are still important effects to be accounted for.

The paper is arranged as follows. The theory of the loss of energy by β -particles is discussed in § 2. The classical theory is first briefly described and then the calculations made by Gaunt on the quantum theory. The distribution of the loss of energy required by Gaunt's calculations is considered, and in particular an approximate expression for the primary ionisation is deduced. The extension of Gaunt's results to fast β -particles is also considered. A summary of the previous investigations on the phenomena which bear on the distribution of the loss of energy is given at the beginning of § 3. The rest of this section is devoted to the comparison of theory and experiment.*

§ 2. *Theory.*

The classical theory of Bohr† hinges on the concept of "time of collision" and the relation of this quantity to the natural period of atomic electrons. The collision of a β -particle with an electron theoretically starts when the β -particle is at an infinite distance from the electron on one side and lasts until it is at an infinite distance on the other side. However, the effect on the electron takes place, for all practical purposes, in the time the β -particle takes to travel a distance comparable with the distance of the electron away from its path, i.e., a time of the order of p/v , where p is the "impact parameter" and v is the velocity of the β -particle. This is the time of collision in Bohr's theory. If this is small compared with the natural period of the atomic electron the latter behaves

* The main results arrived at in this paper were first described by the writer in a dissertation presented for the degree of Ph.D. of the University of Cambridge (1929).

† 'Phil. Mag.,' vol. 25, p. 10 (1913); vol. 30, p. 581 (1915).

during the collision as if it were free and the energy acquired by it is given by the classical formula for free electrons, viz.,

$$Q = (2e^4/mv^2)/(p^2 + a^2), \quad a = 2e^2/mv^2. \quad (1)$$

If the time of collision is appreciably greater than the natural period, i.e., if p is appreciably greater than v/v where v is the natural frequency of the atomic electron, the conditions are practically adiabatic and there is no transfer of energy. The total energy lost by a β -particle in traversing matter is therefore on the classical theory given by taking Q equal to 0 for values of p greater than a certain quantity p_r , which is of the order of v/v ; and equal to the value given by (1) for smaller values of p . Thus

$$\frac{dT}{dx} = \int_{p=0}^{p=p_r \approx v/v} \frac{2e^4}{mv^2} \frac{2\pi p dp n}{p^2 + a^2} = \frac{4\pi n e^4}{mv^2} \log \left(\frac{p_r \approx v/v}{a} \right) \quad (2)$$

where n is the number of electrons per unit volume. Bohr calculated the exact value of the effective upper limit p_r and found

$$p_r = (1.123/2\pi)v/v. \quad (3)^*$$

Substituting this value in (2) and also substituting for a its value given by (1) we find

$$(dT/dx)_{\text{Bohr}} = (4\pi n e^4/mv^2) \log (1.123 mv^2/4\pi v e^2). \quad (4)$$

Before proceeding further it is desirable to express the above results in terms of Q instead of the impact parameter p . The connection between the two is given by (1). It follows from this equation that the average number of collisions per centimetre of its path in which the β -particle loses energy between Q and $Q + dQ$ in traversing free electrons is given by

$$\phi_0(Q) dQ = (2\pi n e^4/mv^2) dQ/Q^2 = (k/\beta^2) dQ/Q^2 \quad (5)$$

(β representing v/c). The rate of loss of energy given by (4) is then in terms of Q as variable expressed by

$$\frac{dT}{dx} = \int_{Q=Q_r}^{Q=mv^2/2} Q \frac{k}{\beta^2} \frac{dQ}{Q^2} = \frac{k}{\beta^2} \log \left(\frac{mv^2/2}{Q_r} \right), \quad (6)$$

Q_r is the effective lower limit to the values of Q for which (5) is applicable. It corresponds to the limit p_r of p and is given by (1) provided we substitute p_r for p . Thus

$$Q_r = \frac{2e^4}{mv^2} \left(\frac{2\pi}{1.123} \frac{v}{v} \right)^2. \quad (7)$$

* If the frequency of the atomic electron is so high and the size of its orbit so large, that v/v is less than the latter then p_r loses the significance it has in Bohr's theory. This is why Bohr's formula is not applicable to slow particles and heavy atoms.

We shall take v in this formula equal to the ionisation potential, J , of the electrons, divided by h ; and also substitute βc for v . (7) then becomes

$$Q_v = (8\pi^2 e^4 / 1 \cdot 123^2 mc^4 h^2) J^2 / \beta^4 = k' J^2 / \beta^4. \quad (7A)$$

The above formulæ apply only to velocities small compared with that of light. The influence of "relativity effects" on the collisions between β -particles and electrons was considered by Bohr in his second paper on the subject (1915). He showed that for free electrons, provided the velocity acquired is small compared with that of the β -particle, these effects leave the formula (1) for Q unaltered. It is worth while considering the general reason for this result. The field of the β -particle suffers a Fitzgerald contraction, which may be regarded as a concentration of the lines of force near the plane through the particle and perpendicular to its direction of motion. The time of collision of a fast β -particle with an electron at a given distance away is thus much less than it would be if the lines of force spread out uniformly in all directions, being reduced by the factor $(1 - \beta^2)^{-\frac{1}{2}}$. The concentration of the lines of force, however, produces a corresponding increase in the electric intensity, the force acting on the electron during the collision, in a direction normal to the path of the β -particle, being increased by $(1 - \beta^2)^{-\frac{1}{2}}$. As a result the *time-integral* of the force on the electron is unaltered.* The velocity acquired by an electron (if small compared with c) depends only on the time integral of the force acting on it, so that for free electrons, which are acted upon only by the moving particle the value of Q is unaltered by relativity effects and is therefore given by (1).

It is a very different matter when the atomic binding forces play a part during the collision. We have seen that in that case the time of collision becomes an important factor and however big the time integral of the force due to the moving particle may be, there is little transfer of energy if the time of collision is much larger than the natural period of the electron. By reducing the time of collision the relativity effect increases the range of action of the β -particle and the value of p for which the time of collision is comparable with the natural period is increased by $(1 - \beta^2)^{-\frac{1}{2}}$; the new value of p , being $(1 \cdot 123 v / 2\pi\nu) \times (1 - \beta^2)^{-\frac{1}{2}}$. This does not represent the full relativity correction to the effect of the binding forces since a small part of the loss of

* It is assumed that the displacement of the electron during the collision is small compared with the impact parameter and that the mass of the electron is constant. These conditions are satisfied provided the velocity acquired by the electron is small compared with that of the β -particle.

energy represented by Bohr's formulæ is due to the component of the force of the β -particle parallel to its motion.* The value of p_r fully corrected is given by

$$\log p_{rR} = \log (1 \cdot 123 v/2\pi v) + \frac{1}{2} \log (1 - \beta^2)^{-1} - \frac{1}{2} \beta^2. \quad (8)$$

The corresponding value of Q_r is obtained by substituting p_{rR} in (1), and is given by

$$\log Q_{rR} = \log (k'J^2/\beta^4) + \log (1 - \beta^2)^{-1} - \beta^2. \quad (9)$$

In the case of fast β -particles we shall only require the rate of loss of energy $d_w T/dx$ in collisions for which Q is less than a certain quantity W which is much less than T and much greater than Q_r . W therefore occurs in a region of values of Q for which the electrons behave as if they were free and for which the velocity acquired by them is small compared with that of the β -particle. Under such conditions the expression (5) for $\phi(Q)$ holds and the value of $d_w T/dx$ is given by substituting W for the upper limit of Q in (6) and substituting Q_{rR} for Q_r . We then have

$$d_w T/dx = (k/\beta^2) \log (W/Q_{rR}) = (k/\beta^2) \{ \log (W/k'J^2) + \log (\beta^4/\overline{1 - \beta^2}) - \beta^2 \}. \quad (10)$$

Quantum Theory.—The value of $\phi(Q)$ for free electrons is the same on the quantum theory as on the classical theory except for values of Q comparable with the energy of the β -particle—a region which does not concern us much here. This region was investigated by N. F. Mott† and his results were considered in a recent paper by the writer‡ in relation to the number of branches produced by slow β -particles, and found to be in satisfactory agreement with the observations.

The inelastic collisions of β -particles with atomic electrons, involving the effect of atomic forces, was considered by Born§ in 1926 and later by Gaunt.|| Born only considered one or two cases of excitation and the calculations which are most useful for our present purpose are those of Gaunt.

Gaunt applied the quantum theory to distant collisions, i.e., collisions for which the impact parameter p is greater than atomic dimensions, and in which

* For this component, though the time of collision is decreased by $(1 - \beta^2)^{-\frac{1}{2}}$ the intensity of it is not correspondingly increased.

† 'Proc. Roy. Soc.' A, vol. 126, p. 259 (1930).

‡ 'Proc. Roy. Soc.,' A, vol. 128, p. 459 (1930).

§ 'Z. Physik,' vol. 38, p. 803 (1926).

|| 'Camb. Phil. Soc. Proc.,' vol. 23, p. 732 (1927).

the β -particle may be assumed to move undisturbed in a straight line.* The important result which Gaunt's calculations lead to is that when the time of collision is small compared with the natural period of the atomic electron the average energy transfer, $\bar{Q}$, according to the new quantum theory, is the same as the classical value of Q given by (1).† When the time of collision is much greater than the natural period (i.e., $p \gg p_c$) the conditions are adiabatic and there is of necessity no loss of energy. It follows that in the distant collisions considered by Gaunt the average loss of energy and the restriction to it imposed by atomic forces, is practically the same as on the classical theory of Bohr. In order to obtain a formula for the loss of energy due to *all* collisions Gaunt made the assumption that the classical formula also applies to the close collisions, for which the impact parameter is of the order of or less than atomic dimensions.‡ His final formula is in consequence for all practical purposes the same as Bohr's classical formula.

Gaunt's calculations were made for particles with velocities small compared with that of light. In his calculations the reaction of the atomic electron on the moving particle is neglected and the latter is assumed to move undisturbed in a straight line during the collision. Therefore in order to extend his calculations to β -particles with velocities comparable with that of light it is not

* Gaunt's calculations are based on the treatment of dispersion and absorption by Dirac. They bear a relation to the quantum theory of dispersion similar to the relation of Bohr's calculations to the classical theory of dispersion.

† Gaunt himself does not use the conception of time of collision but the quantity " u " which occurs in his calculations is of the order of $Jp/hv = vp/v$, and therefore represents the ratio of the time of collision to the natural period of the atomic electron. This interpretation of u immediately leads to the interpretation of Gaunt's results given above.

‡ The argument in favour of this assumption regarding close collisions may be based on the following points:—(1) Gaunt's calculations extend to values of p for which the average energy lost per collision is not affected by binding forces, so that for closer collisions we would expect these forces *a fortiori* not to affect the energy loss; (2) except for large values of Q (comparable with T) the classical and quantum formulæ for free electrons are the same. In view of the fact that Bohr's formula differs appreciably from experiment it is worth while to point out two criticisms of this argument. In the first place, for the smallest values of p dealt with by Gaunt the binding forces, though they may not affect the average energy lost per collision, still have a large effect on the energy losses in individual collisions; these losses being either zero or large enough to excite or ionise the atom. It is therefore misleading to think that Gaunt's calculations take us to a region of values of p for which the binding forces cease to have an effect, and to which formulæ for free electrons necessarily apply. Secondly, the results of the new quantum theory of collisions with free electrons cannot be expressed in terms of impact parameter, whilst in order to include the close collisions to which the above assumption applies we have to integrate with respect to the impact parameter down to $p = 0$.

necessary to use relativistic quantum mechanics. All we have to do is to allow for the different variation of the perturbing potential with time, *i.e.*, for the decrease in the time of collision which results from the Fitzgerald contraction of the field of the moving particle. Now the calculations of Gaunt for slow particles show that as far as the time of collision is concerned it affects the energy lost in distant collisions in practically the same way on the quantum theory, as on the classical theory. It is therefore very likely that a calculation of the loss of energy by fast β -particles, parallel to that made by Gaunt for slow particles would lead to the same relativity correction to the energy lost in distant collisions as that required by classical theory. This certainly applies to the term $(1 - \beta^2)^{-1}$ which is the more important and interesting part of the correction. If we therefore assume, as Gaunt did for slow particles, that the energy lost in close collisions is also given by the classical formulæ then the entire formula for the loss of energy by fast β -particles is the same as the classical formula (10).

We shall now consider the distribution of the loss of energy between different kinds of collisions. As mentioned in the introduction this distribution brings out the fundamental difference between the classical and quantum theories. On the quantum theory all the energy is lost in quantities which are at least sufficient to ionise or excite the atoms traversed. On the classical theory on the other hand there is no lower limit to the energy which may be lost in a collision and the greater part of the energy is in fact lost in quantities which are much less than the ionisation and excitation potentials of the atoms traversed. Since the total energy lost in all collisions is nearly the same on the two theories it follows that the energy lost in ionisation and excitation is much greater on the quantum theory than on the classical theory. This important result may conveniently be represented graphically as in fig. (1). The abscissæ represent $\log Q$ and the ordinates the values of $\phi(Q)$ in terms of the classical value, $\phi_0(Q)$, of $\phi(Q)$ for free electrons (initially at rest), which is given by (1). This, as we have already pointed out, is also the value of $\phi(Q)$ for free electrons given by the quantum theory (except for Q close to T), so that the departures from $\phi_0(Q)$, *i.e.*, from unit ordinate, show the effect of atomic forces, whether we are thinking of the classical or quantum theory. Since $\phi(Q)$ according to (1) is proportional to $1/Q^2$, the loss of energy between any two values of Q is proportional to the area under the curves. The curve *cl* represents the classical theory and the curve *qu* the quantum theory. The energy lost on the classical theory in quantities less than the first resonance potential, R , is represented by the area *abnfa*, the limit *ab* which represents the

effect of binding forces, being determined by the value of Q_v . On the quantum theory no energy is lost in quantities less than R so that the curve qu comes to

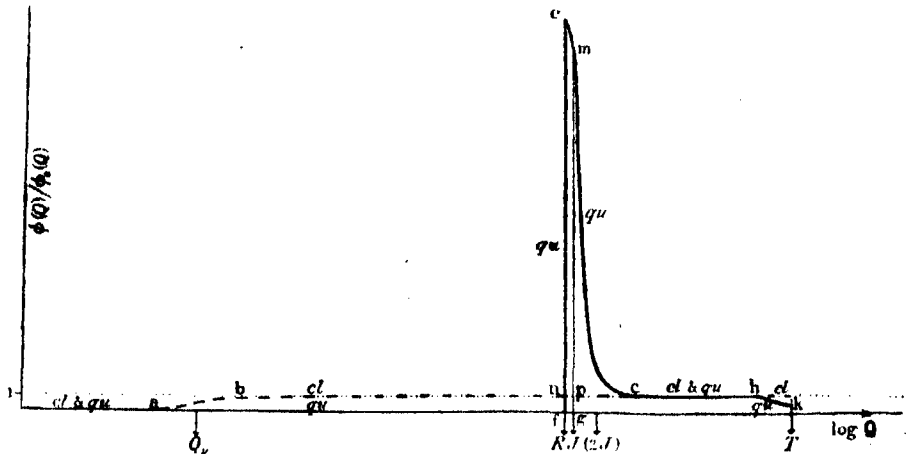


FIG. 1.— $\phi(Q)$ for Atomic Electrons (one energy level).

—, quantum theory. - - - - -, classical theory., $\phi_0(Q) = (2\pi e^4 n / mv^2) / Q^2$.

zero at that point.* Now since the total energy lost is the same on the two theories, the area under qu is equal to the area under cl so that $nemcn = abnfa$. Gaunt only dealt with distant collisions, and the exact shape of $nemc$ cannot be obtained from his calculations. However, as far as his calculations permit us to go, the loss of energy represented by the area $nemcn$ is roughly divided in the ratio 5 : 4 between excitation and ionisation, and the amount spent in ionisation is confined to collisions in which Q is close to J , the two curves qu and cl agreeing for values of Q greater than about $2J$.† (The part hk of qu represents the falling off in the frequency of violent collisions required by Mott's calculations for collisions with free electrons.)

Q_v decreases with increasing velocity (equation (7A)) so that the area $abnfa$ and therefore $pmcp$ increases with the velocity. The excess of the energy spent in ionising collisions over the classical value is accordingly greater the greater the velocity.

Since the "excess" energy represented by the area $pmcp$ is confined to a region of values of Q close to J the exact number of ionising collisions I_v' , to which it corresponds, does not depend very much on the actual shape of this

* The discreteness of the excitation losses is not shown in the figure.

† It might be pointed out that since $\phi_0(Q)$, which is taken as unit ordinate in the figure, varies as $1/Q^2$ the increase in the frequency of collisions as Q approaches J , which is required by the quantum theory, is very pronounced.

area. In virtue of this it is possible to obtain an approximate formula for I'_q provided we use the result that the energy represented by *pmcp* is approximately four-ninths that represented by *abnfa*. It is found in this way that

$$I'_q \approx I_{cl.} \times 0.4 \log (J/Q_v),$$

where $I_{cl.}$ is the total number of ionising collisions (or primary ionisation), according to the classical theory. I'_q is the excess of the number of ionising collisions over the classical number. The total primary ionisation corresponding to the quantum theory calculations of Gaunt is therefore given by

$$I_q \approx I_{cl.} \{1 + 0.4 \log (J/Q_v)\} \approx I_{cl.} \times 0.4 \log (12J/Q_v). \quad (11)$$

Substituting for $I_{cl.}$ its value, viz.,

$$I_{cl.} = (2\pi e^4 n / mc^2) / J\beta^2 = k / J\beta^2 \quad (12)$$

and for Q_v its value given by (9), (11) becomes

$$I_q \approx \frac{k}{J} \frac{0.4}{\beta^2} \left\{ \log \left(\frac{12 \beta^4}{k'J} \right) + \log (1 - \beta^2)^{-1} - \beta^2 \right\}. \quad (11A)$$

We see that $I_{cl.}$ varies as β^{-2} but owing to the term within brackets in (11A), which increases with the velocity, I_q varies as an inverse power of the velocity less than 2.

The primary ionisation by β -particles with very great energy is especially interesting. The term $\log (1 - \beta^2)^{-1}$ inside the brackets in (11A) has a predominant effect when β is close to unity, and for such velocities the primary ionisation increases with increasing velocity, in contrast with the normal variation. If we substitute for k' in (11A) its numerical value given by (7A) we find that I_q in fact passes through a minimum at a velocity of about 0.97 c., and then starts to increase reaching a value for β -particles with energy of about 10^9 volts roughly 50 per cent. greater than the minimum value at 0.97 c.* We cannot easily deny this result on theoretical grounds, for it

* According to this result the cloud tracks of the β -particles associated with penetrating radiation should be denser than those of the fast β -particles from known radioactive substances.

10^9 volts corresponds to a velocity of 0.99999990 c. and for the same impact parameter the time of collision for such a particle is about 50 times less than the time of collision for a β -particle with a velocity of 0.97 c., owing to the greater Fitzgerald contraction of the first particle. Hydrogen atoms at a distance of 3×10^{-4} cm. from the path of the first particle receive energy freely, the time of collision being about seven times less than the natural period of the hydrogen electron. For the same distance away from the second particle the conditions are however practically adiabatic the time of collision being about seven

follows directly from the Fitzgerald contraction and the fact that for bound electrons a large force for a short time is more effective than a small force for a long time—effectiveness on the quantum theory necessarily meaning excitation and ionisation.

The distribution curves in fig. 1 refer to an atom with only one energy level. For an atom with several energy levels the quantum theory curve has several “humps” or “peaks” similar to *nemc* in fig. 1, and the general shape of the resultant curve for an atom with 3 energy levels, say (such as oxygen) is shown by the full curve in fig. 2. The corresponding value of $\phi(Q)$ on the classical

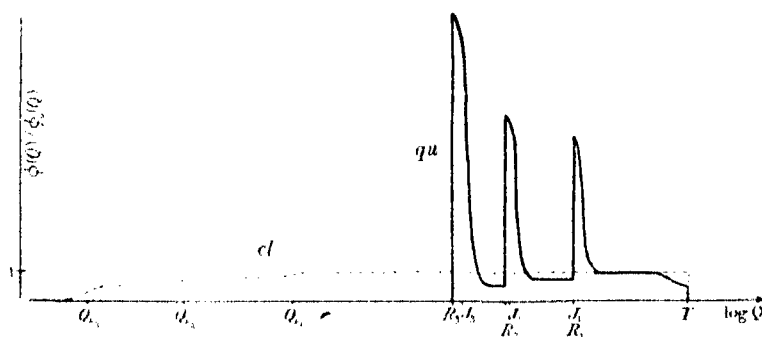


FIG. 2.— $\phi(Q)$ for Atoms with 3 Energy Levels (occupied). Twice as many electrons in outer level (J_3) as in inner levels.

—, quantum theory. ----, classical theory., $\phi_0(Q) = (2\pi Ze^4/mv^2)/Q^2$.

theory is represented by the “broken” curve in the same figure. Owing to the small interval between the resonance potential and the ionisation potentials for the inner atomic electrons, it is unlikely that much energy is spent in the excitation of these electrons. The part *nemp* of the curve *qu* in fig. 1 may, therefore, not be represented in the case of many-electron atoms, except for the outer electrons. Gaunt’s calculations were, of course, made for atomic electrons which can make transitions freely to any higher level, and what

times greater than the natural period. It is interesting that the extra number of ions produced by the first particle are produced at distances from its path between about 10^{-5} cm. and 5×10^{-4} cm. The *theoretical* thickness of the Wilson track of the first is therefore greater than that of the second. This thickness is independent of any scattering and diffraction effects, which decrease with increasing velocity. A β -particle with energy as large as 10^{12} volts would produce an appreciable number of ions at distances away from its main path up to about 1 cm. (in oxygen about three primary ions would be produced per cm. of path at distances from the path between 0.5 cm. and 1 cm.—with equal numbers between 0.25 and 0.5 cm., and between 0.125 and 0.25 cm., etc.).

happens when these levels are occupied is therefore at present a matter of conjecture. Apart from this uncertainty the curve qu in fig. 2 probably represents correctly the general form of the function $\phi(Q)$ for many-electron atoms required by the quantum theory. The important results which it represents is that the frequency $\phi_q(Q)$ of collisions in which the loss of energy, Q , is close to but greater than an ionisation potential of the atom, is much greater than the classical value of $\phi(Q)$; and that the electrons in any given level experience no inelastic collisions in which the energy lost is less than the resonance potential for that level.

§ 3. *Experimental Results and Comparison with Theory.*

As mentioned in the introduction information about the distribution of the loss of energy by β -particles between different kinds of collisions may be obtained from observations on the ionisation, straggling, and frequency of "branches," since these phenomena depend on collisions for which Q is confined to a small range of values.

The magnitude of the primary ionisation is the number of ions produced by the direct action of the β -particle per centimetre of its path. It depends mainly on collisions for which Q is greater than but close to the ionisation potential of the outer electrons in the atoms traversed. Observations on the primary ionisation produced by slow β -particles traversing air were made by C. T. R. Wilson* and on fast β -particles with velocities between about 0.5 c. and 0.96 c., traversing hydrogen and oxygen, by F. R. Terroux and the writer.†

By straggling is meant the different amounts of energy lost by β -particles in travelling the same distance, or alternatively the different distances travelled in losing the same amount of energy. Observations on the straggling of the ranges of slow β -particles, i.e., on the distribution of ranges of β -particles with the same initial energy, were recently made by the writer‡; and on the straggling of fast β -particles by thin foils by White and Millington.§ The results of these observations have been interpreted in terms of $\phi(Q)$ by means of a theory of straggling recently given by the writer.|| The results obtained for slow β -particles give information about the frequency of the collisions for which Q is of the order of 500 volts. The results for fast β -particles give the

* 'Proc. Roy. Soc.,' A, vol. 104, p. 1, 192 (1923).

† 'Proc. Roy. Soc.,' A, vol. 126, p. 289 (1930).

‡ 'Camb. Ph.D. Thesis' (1929).

§ 'Proc. Roy. Soc.,' A, vol. 120, p. 701 (1928).

|| 'Proc. Roy. Soc.,' A, vol. 125, p. 420 (1929).

effective value of ϕ (Q) for a range of values of Q from about 500 to 2000 volts.

The number of "branch tracks" in a cloud photograph gives directly the frequency of collision ϕ (Q) for values of Q from about 3000 volts upwards. The lower limit is set by the size of the smallest branch which can be detected and measured. Observations on the number of branches produced by slow β -particles in oxygen were recently made by the writer,* and by fast β -particles in oxygen by the writer in collaboration with F. R. Terroux.*

The results of the above investigations are summarised in the following table. They are given in terms of the ratio of the experimental values of ϕ (Q) to the classical values, ϕ_0 (Q), given by (5). This equation refers to free electrons. The values of Q dealt with here are, however, such that on the classical theory the binding forces play no part in the corresponding collisions and (5) is therefore applicable.†

Table I.—Ratio of Observed Values of ϕ (Q) for Light Elements to ϕ_0 (Q).

$$[\phi_0(Q) = (2\pi NZe^4/mv^2)/Q^2]$$

Velocity of β -particles.	Q (volts).	ϕ (Q) _{obs.} : ϕ_0 (Q).	Phenomenon investigated.
Slow β -particles $v \approx 0.25$ c.	20	2.5	Primary ionisation Straggling of ranges Frequency of branches
	500	1.7	
	4000	0.9	
	$\left\{ \int_0^{T/2} Q\phi(Q) dQ \right\}_{\text{obs.}} \approx 0.65 \left\{ \int_0^{T/2} Q\phi(Q) dQ \right\}_{\text{Bohr}}$		Stopping power
Fast β -particles $v \approx 0.75$ c.	20	5.0	Primary ionisation Straggling in foils Straggling in foils Frequency of branches Frequency of branches
	500	2.3	
	2000	2.3	
	7500	2.1	
	2500	1.9	
	$\left\{ \int_0^{10,000} Q\phi(Q) dQ \right\}_{\text{obs.}} \approx 0.7 \left\{ \int_0^{10,000} Q\phi(Q) dQ \right\}_{\text{Bohr}}$		Stopping power

* *Loc. cit.*

† (5) neglects the motion of the atomic electrons. Though taking this motion into account reduces somewhat the difference between classical theory and experiment, it does not remove the more serious discrepancies. We are, however, not specially concerned with the exact requirements of classical theory in this paper and the classical formulae which are adopted are those which serve as the most convenient and definite parameters for discussing the results.

The first thing we notice about the results given in the above table is that whilst the observed values of the rate of loss of energy, represented by $\int Q\phi(Q)dQ$ are actually somewhat less than the classical values, the observed values of $\phi(Q)$ for the values of Q dealt with, are much greater than the classical values. The excess of $\phi(Q)$ over the classical values is moreover much more pronounced for fast β -particles than for slow β -particles. The results for the primary ionisation and frequency of branches essentially refer to ionising collisions. The values of Q in the cases of straggling are also greater than the majority of the ionisation potentials of the matter traversed, and are not much less than the largest. The results therefore mean that the number of collisions in which the energy lost is of the order of or greater than the ionisation potentials of the atoms traversed, is much greater than the number required by classical theory, the excess increasing with increasing velocity. This excess and the fact that the *total* loss of energy is somewhat less than the classical value imply a third result, viz., that the loss of energy in collisions for which Q is appreciably less than the ionisation potential, is only a small fraction of that required by Bohr's classical theory. In the case of fast β -particles, for instance, we can set an upper limit to this fraction of about one-fifth. These results show that the failure of the classical theory is far more pronounced when we consider the distribution of the loss of energy between different kinds of collisions, than when we consider its average value for all collisions. This state of affairs is just what is required by the quantum theory. We saw in § 2 that whilst this theory requires approximately the same total loss of energy as the classical theory, it requires it to be all spent in excitation and ionising collisions. As a result it gives at least a qualitative explanation of why the energy lost in collisions for which Q is of the order of or greater than the ionisation potential is considerably in excess of the classical requirements. Moreover, as explained in § 2, the excess of the number of ionising collisions over the classical values demanded by the quantum theory is greater the greater the velocity of the β -particles, and this is also in agreement with the experimental results. We shall now proceed to consider more closely the relation between the experimental results and the requirements of the quantum theory, to see to what extent the agreement between them is quantitative.

The phenomenon of primary ionisations is the one which gives the most crucial results. We shall first consider the relation between the variation of the primary ionisation with velocity and that of the observed rate of loss of energy with velocity. In requiring all the energy to be lost in ionisation and

excitation collisions the quantum theory requires this relation to be much more intimate than it is on the classical theory.

In the preceding paper the rate of loss of energy $d_w T/dx$ by fast β -particles due to collisions for which $Q < W = 1500$ volts is considered. The theoretical formula for this quantity on the classical and quantum theories is given by (10), viz.,

$$d_w T/dx = (k/\beta^2) \log (W/Q_{iR}) = (k/\beta^2) \{ \log (W/k' \bar{J}^2) + \log (\beta^4/1 - \beta^2) - \beta^2 \}. \quad (10A)$$

The classical formula for the primary ionisation is

$$I_{cl.} = k/J\beta^2. \quad (12)$$

The formula derived in § 2 for I , according to the quantum theory, is

$$I_q = 0.4 (k/J\beta^2) \{ \log (12/k'J) + \log (\beta^4/1 - \beta^2) - \beta^2 \}. \quad (11A)$$

The similarity between (10A) and (11A) is due to the circumstance already mentioned, viz., that all the energy is, on the quantum theory, spent in ionisation and excitation, an approximately constant fraction being spent in ionisation.* The values of J , $\bar{J}$ and W in the cases concerned here, are such that the two log terms (in (10A) and (11A) respectively) are practically of the same magnitude and therefore vary with the velocity in the same way. The theory therefore requires the primary ionisation and $d_w T/dx$ to obey practically the *same velocity law*. The observed variation of $d_w T/dx$ with velocity is given by equation (18) in the preceding paper, viz.,

$$d_w T/dx = 1.06 \beta^{-1.4 \pm 0.05}. \quad (13)$$

This applies to a range of velocities from about 0.5 c. to 0.96 c. The observations of Williams and Terroux on primary ionisation were made for the same region of velocities. According to their results:—

$$\left. \begin{aligned} I_{obs.} &= 5.2 \beta^{-1.5 \pm 0.2} \text{ for hydrogen} \\ I_{obs.} &= 22 \beta^{-1.1 \pm 0.2} \text{ for oxygen} \end{aligned} \right\}. \quad (14)$$

The mean power of β is -1.3 and agrees satisfactorily with the velocity law for $d_w T/dx$. As far as they go the experimental results, therefore, bear out satisfactorily this crucial requirement of the quantum theory.

* On the classical theory the variation with velocity of the log term in (10A) is connected with the effect of binding forces on the number of collisions in which the energy lost is of the order of Q_v . Q_v is negligible compared with the ionisation potentials and the variation of the log term, therefore, does not concern the number of ionising collisions on the classical theory.

The absolute theoretical values of the primary ionisation according to (11A) may be evaluated since all the terms are known. It is found that for a velocity of 0.75 c. the primary ionisation according to the quantum theory is about nine times the classical value, whilst it varies approximately as $\beta^{-1.7}$. The observed values for $\beta = 0.75$ are about five times the classical values and vary as $\beta^{-1.3}$. Thus, though the quantum theory formula derived from Gaunt's calculations explains the general nature of the difference between the observed values and the classical values it does not give correctly the actual magnitude of this difference. This is of course not surprising, since we found in the preceding paper that the quantum theory formula (10A) for $d_w T/dx$ fails in a similar manner. In this connection it is very significant and satisfactory that if the value of the constant k' which occurs inside the "log" terms in the above formulæ be properly adjusted, these formulæ fit with the experimental results for primary ionisation and rate of loss of energy both as regards absolute magnitude and variation with velocity.

We shall now consider the results for the other phenomena represented in Table I. With one exception the values of $\phi(Q)$ deduced from observations on these phenomena are greater than the classical values. Now as far as calculations have been made, the values of $\phi(Q)$ on the quantum theory exceed the classical values only for values of Q in the neighbourhood of ionisation potentials, as is shown in fig. 2. Therefore it is only by associating the values of Q , upon which these phenomena depend, with values of J for the atoms traversed that we can hope to explain the excess of $\phi(Q)$ over the classical value. In the case of primary ionisation the values of Q concerned are essentially close to an ionisation potential and in virtue of this the quantum theory gives, as we have just seen, a general explanation of the large excess of the primary ionisation over the classical value. There is, however, no essential connection between the values of Q , upon which the *other* phenomena dealt with depend, and the ionisation potentials of the atoms traversed, and in one case at least the results must be left unexplained.

In the case of the straggling of slow β -particles the values of Q upon which the phenomenon depends are of the order of 500 volts. The experiments were made on β -particles traversing oxygen and the k electrons of this element have an ionisation potential of about 500 volts. The value of $\phi_q(Q)$ for these electrons is therefore much greater than the classical value for Q close to but greater than 500; whilst for smaller Q the value of $\phi_q(Q)$ for the k electrons is of course zero. If we assume that $\phi_q(Q)$ for $Q > 500$ exceeds the classical value by a constant factor between $Q = 500$ and $Q = 1000$ then this factor is about 7.

Only 25 per cent. of the electrons in oxygen are in the k level so that the average value of $\phi_q(Q)$ in this region for the whole atom is about $2\frac{1}{2}$ times the classical value. For smaller values of Q it is three-quarters the classical value. The straggling corresponding to this distribution of $\phi(Q)$ is appreciably greater than the classical straggling. The actual straggling corresponding to it has not been calculated in detail, but it is roughly of the same order of magnitude as the observed straggling, which corresponds to a value of $\phi(Q)$ about 1.7 times the classical value for Q between about 250 and 1000 volts.*

The observations on the frequency of branches by slow β -particles were also made on β -particles traversing oxygen. The values of Q concerned in this case are, however, much greater than the ionisation potential of the k electrons of this element and the quantum theory therefore requires no excess over the classical value of $\phi(Q)$. In fact the values of Q for branches are comparable with the energy of the β -particle, and according to the calculations made by Mott for free electrons the values of $\phi_q(Q)$ for such values of Q are less than the classical values. We see from the table that the observed value of $\phi(Q)$ is also less than the classical value. The experimental results for branches are more detailed than is represented in the table and a more complete comparison with theory which was recently made by the writer,† shows that the requirements of the quantum theory agree with the observations within the experimental error of about 10 per cent.

We shall now consider the results for straggling and branches in the case of fast particles. The results for straggling refer to β -particles traversing mica the composition of which is approximately represented by the chemical formula $K_2O, 3Al_2O_3, 6SiO_2, 2H_2O$. According to this formula about 20 per cent. of the electrons in mica have ionisation potentials, J , of about 500 volts and greater, and for 8 per cent. of the electrons J is greater than about 2000 volts. The highest value of J is that of the k electrons of potassium which is about 4400 volts. Thus, though the majority of the electrons in mica have ionisation potentials much less than the values of Q to which the results for straggling refer, there are a few with ionisation potentials in this region. As a result the straggling according to the quantum theory is greater than the classical straggling, and this may account for the excess of the observed straggling over the classical value for the smaller values of Q concerned. However, as Q increases the value of $\phi(Q)$ on the quantum theory approaches the classical

* The value of $\phi(Q)$ deduced from observations on the straggling of ranges are, of course, only effective values for a fairly big region of values of Q .

† *Loc. cit.*

value because there are fewer electrons in mica with large values of J (of the order of 2000 volts) than there are with smaller values of J . The observed values of $\phi(Q)$ on the other hand are as much greater than the classical values for large values of Q as they are for small values of Q . Indeed, we see from the table that this excess is maintained in the region of much larger values of Q which are concerned in the results for "branches." In the latter case the largest ionisation potential of the element traversed (oxygen) is negligible compared with the values of Q . Atomic forces therefore play no part and we are led to the conclusion that the excess of $\phi(Q)$ over the classical value, $\phi_0(Q)$, in the case of the production of branches by fast β -particles, and to some extent in the case of the straggling of fast β -particles, must be attributed to an effect which concerns the collisions of fast β -particles with *free* electrons. The only possible effect is a relativity effect (with its attendant 'spin' effect), since apart from that the value of $\phi(Q)$ required by the new quantum theory for β -particles traversing free electrons, is definitely known, and is equal to the classical value of $\phi(Q)$ for free electrons, *i.e.*, $\phi_0(Q)$.* If the observed excess of $\phi(Q)$ over $\phi_0(Q)$ in the case of the production of branches by fast β -particles is a relativity effect, it should be more pronounced the greater the velocity. Actually the observed value of $\phi(Q)$ in the case of branches is about $2\frac{1}{2}$ times $\phi_0(Q)$ for $\beta = 0.9$, and about $1\frac{1}{2}$ times $\phi_0(Q)$ for $\beta = 0.7$; whilst for slow β -particles with $\beta = 0.2$ there is no excess, the observed and theoretical values of $\phi(Q)$ agreeing within experimental error. As far as these results go they bear out the supposition that the effect under consideration is a relativity effect. Whether the new quantum mechanics will lead to the right relativity correction or whether, for instance, it will leave $\phi(Q)$ unaltered at high velocities as does the classical theory, is of course another question.

In admitting a relativity correction to $\phi(Q)$ for the large values of Q such as those concerned in the production of branches we are confronted with another question, *viz.*, does this relativity effect exist to the same extent for small values of Q such as those concerned in primary ionisation? If it does, then the excess of the observed primary ionisation over the classical value which we have attributed to the effect of atomic forces, is partly due to relativity effect. In that case the excess which results from atomic forces becomes less significant. It will therefore be more satisfactory if the relativity correction to the quantum theory formula for free electrons turns out to be appreciable only for large

* Except for Q comparable with the energy of the β -particle, which does not concern us here.

values of Q . In connection with the significance of the effect of atomic forces on the primary ionisation it is, however, worth while to point out that the important departure from the classical velocity-law ($I \propto \beta^{-2}$) is maintained in the region of small velocities, where there can be no relativity effect.

§ 4. Summary.

The theory of the loss of energy by β -particles is discussed. The classical and quantum theories require approximately the same average rate of loss of energy but they differ radically as regards the distribution of the loss of energy between different kinds of collisions. The experimental results arrived at in previous investigations and which are summarised in this paper afford a fairly comprehensive test of the theoretical requirements. It is found that the quantum theory is in general agreement with experiment, and that it gives an explanation of several effects which were previously obscure, particularly in connection with the phenomenon of primary ionisation. The experimental results and their departure from classical requirements, in receiving a general explanation on the quantum theory support to that extent the assumption which underlies Gaunt's calculations, viz., that the laws which govern the perturbation of an atom by the electric force in a radiation field may be applied to the perturbation of an atom by the electric force of a moving charged particle, provided the reaction on the particle is small.

Quantitatively the requirements of the quantum theory are not on the whole in good agreement with experiment. The theoretical rate of loss of energy and primary ionisation are greater than the observed values of these quantities. On the other hand, the observed number of collisions in which the energy lost is so large that all the atomic electrons may be assumed to behave as if they were free, agrees in the case of slow β -particles with the requirements of the quantum theory within experimental error. For fast β -particles the frequency of such collisions is appreciably greater than that required by the non-relativity quantum theory formula and this excess indicates the nature of the relativity correction required of the quantum theory.

[*Note added in Proof.*—In a recent theoretical paper ('*Annalen der Physik*,' vol. 5, p. 325 (1930)) H. Bethe considers the loss of energy by electric particles in passing through matter, using the quantum-mechanical theory of collisions developed by Born in 1926. Born's own calculations for inelastic collisions were not carried far. Bethe's treatment is more complete and he obtains expressions for the rate of loss of energy, &c. Though the

approach to the problem of collisions in Born's theory is radically different from the method used by Gaunt, the general nature of the theoretical results obtained by Bethe and of their departure from classical requirements are the same as those which follow from Gaunt's calculations, and are equally well represented by the distribution curves in figs. 1 and 2. The exact values of the stopping-power, &c., according to Bethe's calculations are however not the same as those required by Gaunt's work. It is satisfactory that their divergence from the latter improves the quantitative relation with experiment. It is hoped to publish in due course a brief note to show this better agreement.]

In conclusion I wish to thank Prof. W. L. Bragg for much helpful discussion and for his continued interest in this work.

*The Chemical Effects of Cathode Rays. Part I.—The
Decomposition of Ammonia.*

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Introduction.

Investigations of the chemical effects of α -particles,* and of low velocity electrons† of known voltages have given valuable quantitative results.

Those investigations using α -particles possess the disadvantage that the power normally available is very small, whilst those using low velocity electrons, though possessing the advantage that the critical potentials for chemical reaction and hence the active species can be determined, are practically limited to low pressures, and to reactions which are not seriously affected by heated filaments. The development of the Lenard tube makes it possible to obtain a very intense source of ionisation, and to investigate reactions over a great

* Lind, "The Chemical Effects of Particles and Electrons."

† Storch and Olson, 'J. Amer. Chem. Soc.,' vol. 45, p. 1805 (1923); Caress and Rideal, 'Proc. Roy. Soc.,' A, vol. 115, p. 684 (1927); Wansbrough Jones, 'Proc. Roy. Soc.,' A, vol. 127, p. 511 (1930).

range of pressures under conditions in which thermal effects are eliminated. It is therefore important to determine how far this method may be rendered quantitative.

McLennan and Greenwood* and Marshall,† using such Lenard tubes operating at about 200 KV., made no measurements on the number or energy of the electrons entering the gas reaction chamber, but by the comparatively large chemical yields obtained by Marshall, together with the accurate analysis of the products, the advantage of this new source of ionisation is readily demonstrated. Attempts to measure the total ionisation were made by Krüger and Utesch‡ and by Marshall; Marshall found it impossible to reach saturation current, and the value for the ionisation arrived at by Krüger and Utesch is almost certainly much too low. Busse and Daniells,§ who investigated the effects of cathode rays on air, oxygen, carbon dioxide and nitric oxide, measured the energy of the electron beam by a calorimetric method, but their results were liable to a large arbitrary correction for radiation from the heated window. The only data available for ionisation by cathode rays are those for air, for which the most reliable value is probably 32.2 ± 0.5 electron-volts per ion pair, independent of the velocity over a large range.|| We are probably justified, however, in assuming that the total ionisation in oxygen relative to air is approximately the same for α -particles and cathode rays. Taking 1.09¶ as the relative total ionisation, we obtain a value of 29.5 electron-volts per ion pair in oxygen. Thus we can calculate from their results the M/N ratios for three reactions, and compare them with the data obtained for α -particles.

Table I.

Reaction.	Calories per molecule.	Volts per molecule.	M/N (cathode rays).	M/N (α -particles).**
$O_2 \rightarrow O_3$	3.4×10^5	18	1.6	1.5-2.6
Air $\rightarrow O_3$	7.8×10^5	35	0.9	2.4
Air $\rightarrow$ Oxides of nitrogen.....	22×10^5	98	0.33	0.77

** Lind and Bardwell, 'J. Amer. Chem. Soc.', vol. 51, p. 2751 (1929).

* 'Proc. Roy. Soc.' A, vol. 120, p. 283 (1928).

† 'J. Amer. Chem. Soc.', vol. 50, p. 3178 (1928).

‡ 'Ann. Physik,' vol. 78, p. 113 (1925).

§ 'J. Amer. Chem. Soc.', vol. 50, p. 3271 (1928).

|| Eiel, 'Ann. Physik,' vol. 3, p. 277 (1929).

¶ Bragg, 'Phil. Mag.,' vol. 13, p. 333 (1907).

Thus the agreement obtained is reasonable as to order of magnitude, and is probably not outside the limits of experimental error.

McLennan, Perrin and Ireton,* who investigated the polymerisation of acetylene, measured the number of electrons entering the reaction vessel with a Faraday cylinder. Taking 10^{-8} cm. as the effective radius of the acetylene molecule, they calculated approximately—

$$\frac{\text{No. of molecules reacting}}{\text{No. of molecules hit}} = \frac{4.9 \times 10^3}{3.77 \times 10^4} = 0.13.$$

A result which would appear to be in serious disagreement with Lind and Bardwell's† result of 20 for M/N for α -particles. However, the effective collision area of a molecule is much smaller for fast moving electrons than for collisions between molecules at ordinary temperatures, and, further, varies with the velocity of the electron, and the mean effective collision area under these conditions is therefore unknown. If, however, we take one of their values for maximum voltage and yield, we can calculate a maximum value for the number of electron-volts per molecule reacting.

Table II.

KV. (maximum).	KV. (maximum after passing window).	Pressure.	Molecules per electron.	Electron-volts per molecule (maximum).
120	89.5	40 cm.	1.51×10^4	5.9

This value will be much too high, since the mean energy of electrons entering the vessel is much less than the maximum. If we assume that the amount of energy required to produce one ion pair in acetylene, relative to air, is the same for cathode rays as for α -particles we can make an estimate of the minimum value of M/N. Taking 1.26 as the total ionisation for acetylene relative to air, we obtain $M/N > 4.4$, and it is therefore not unreasonable to suppose that the true value may be in agreement with Lind and Bardwell's value of $M/N = 20$.

In our investigation an attempt has been made to reduce as far as possible the errors in determination of the energy of the electrons, and so to obtain a reliable value for the number of electron-volts per molecule reacting, which will give M/N as soon as ionisation data are available.

* 'Proc. Roy. Soc.,' A, vol. 125, p. 246 (1929).

† 'J. Amer. Chem. Soc.,' vol. 48, p. 1556 (1926).

The reaction chosen for investigation was the decomposition of ammonia, on account of the fact that it has been extensively investigated under the action of α -particles, in the silent discharge, photochemically and thermally. With α -particles Usher* found that decomposition in a small glass vessel proceeded almost to completion. Wourtzelt† calculated that at ordinary temperatures M/N was equal to 0.8. Hydrazine was found by Bredig, Koenig and Wagner‡ as an intermediate product in the silent discharge. The photochemical reaction has been investigated by a number of authors,§ and their results are discussed later. The thermal reaction proceeds almost to completion on various surfaces, and has been very extensively investigated.||

McLennan and Greenwood (*loc. cit.*) investigated the reaction with cathode rays over a small range of low pressures. They concluded from their results that equilibrium was almost entirely on the side of ammonia formation at 4 mm. and at pressures slightly higher, and was displaced in the direction of more decomposition as the pressure was lowered. It is important to note that if their conclusion were correct, it would be entirely at variance with all results obtained using other sources of ionisation, which have shown that equilibrium is always largely on the side of decomposition.

Experimental Arrangements.

A beam of electrons from a Lenard discharge tube was passed through a thin window of aluminium into a reaction vessel, into which ammonia was introduced at different pressures. The tube—illustrated in fig. 1—contains a hollow cylindrical anode A, in which was centred accurately a metal cathode tube C carrying a tungsten filament W. Electrons emitted from the filament were accelerated between the electrodes and passed through a window of aluminium 0.001 cm. thickness, 4 cm. diameter, supported on a water-cooled grid structure of copper. The energy of the beam of electrons is severely limited by the maximum permissible rise of temperature of the window material, so that it is essential for any chemical investigation with cathode-rays, that the energy distribution over the whole area of the window should be as uniform as possible. This was achieved by substituting for the window foil a glass extension to the

* 'J. Chem. Soc.,' vol. 97, pp. 389, 1193 (1910).

† 'Le Radium,' vol. 11, pp. 289, 332 (1919).

‡ 'Z. Physik Chem.,' A, vol. 139, p. 211 (1928); vol. 144, p. 213 (1929).

§ Warburg, 'Preuss. Acad.,' Berlin, p. 746 (1911); Kuhn, 'J. Chim. Phys.,' vol. 23, p. 52 (1926); Dickinson and Mitchell, 'Proc. Nat. Acad. Sci.,' vol. 12, p. 692 (1926); Bates and Taylor, 'J. Amer. Chem. Soc.,' vol. 49, p. 2438 (1927).

|| *Inter alia* Hinshelwood and Burk, 'J. Chem. Soc.,' vol. 127, p. 1105 (1925).

discharge tube, and there introducing a piece of zinc-sulphide screen so that visual observations could be made of the relative energy-density of the beam,

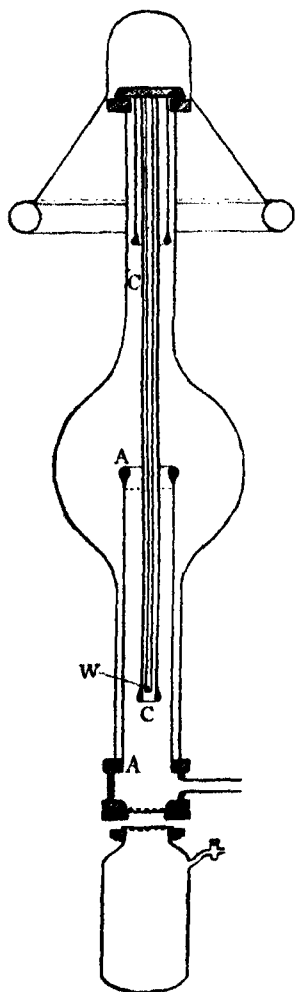


FIG. 1.

as the filament was raised or lowered inside the tubular cathode, and the cathode raised in the anode. Aluminium was chosen for the window because it could be obtained free from minute holes in large sheets rather thinner than it was possible to produce nickel or copper sheets. The electron energy losses in it are only one-quarter of those in the same thickness of the heavier metals, a fact outweighing the higher permissible working temperatures of copper or nickel. It was found that fine pinholes rapidly developed in copper foils at 700°C .—due no doubt to oxidation, and in nickel at 800° to 900°C ., whereas aluminium could be maintained at 600°C . for a long period. An increase in the normal energy losses by a factor of $\times 3$ was possible, using a strong blast of cold air directed on to the window. The foils were clamped into position on the anode by a metal ring and rubber gasket sealed with special low vapour-pressure tap-grease; in this way the windows were very readily replaced. The tube was kept continually evacuated by an oil diffusion pump, so obviating the use of liquid air.

Energy was supplied to the discharge tube at high potential from a large Tesla transformer, the maximum voltage, measured by a 25-cm. sphere gap, being 240 KV. during the investigation. As this form of generator supplies damped alternating currents, all velocities of electrons up to the

velocity corresponding to the maximum voltage on the tube are present in the beam and therefore the energy losses in the window are higher than if the tube were excited by induction coil or direct-current generator. Even with aluminium windows this energy loss limited the chemical investigation considerably.

The total current from the tube cannot be measured by an ammeter placed in the tube circuit as the amount of cold cathode current may be very large in

some tubes ; in any case, the current in the tube is very different from that actually utilised in a gas chamber, so all measurements on the beam were made with Faraday cylinders and calorimeters placed outside the tube. These were facilitated by keeping the anode of the tube permanently earthed and only the cathode at high potential to earth. Electrical leads to all measuring instruments had to be especially earth shielded, to protect them from the strong high-frequency electric field radiating from the Tesla transformer.

The chemical system—illustrated in fig. 2—could be evacuated by means of a mercury diffusion pump, backed alternatively by a Töpler or Hyvac pump,

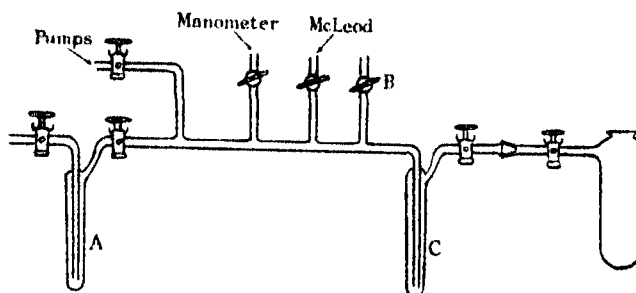


FIG. 2.

the former being used when the products were to be collected. The reaction vessel generally used, was made of pyrex glass, cylindrical in shape, 22 cm. long and 8.5 cm. in diameter. A flange at the top was ground flat, and fitted to the window support. This consisted of a brass disc, bored in hexagonal pattern with 61 holes, each 11/64-inch in diameter, with 3/16-inch spacing between the centres. It was waxed to the vessel and provided with a water-cooling tube. The window consisted of aluminium foil 0.020 mm. in thickness, fixed to the support by means of a cellulose paint which was protected from the action of the rays by a shield of metal. A second vessel, made of soda glass of the same dimensions, and fitted with a window support made to the same plan, was silvered inside to within a few millimetres of the window support, and a platinum wire sealed through the glass making electrical contact with the silver. This vessel could be used as a Faraday cylinder to measure the total number of electrons entering the reaction vessel per second, and also as a reaction vessel. When the pyrex vessel was used, measurements of the current entering the vessel were made before and after exposure by substituting the soda glass Faraday cylinder. It was found that when the filament current and maximum voltage were kept constant, the readings normally agreed to ± 5 per cent.

The Faraday cylinder was connected through a galvanometer to earth. The system of having a separate window for the cathode ray tube and the reaction vessel, was adopted since it was more convenient, and eliminated possible thermal effects on the chemical reactions since the second window remained comparatively cool.

Experimental.

The vessel was first baked out under a high vacuum, the pyrex vessel at about 500° C., and the soda vessel at about 350° C. After this it was exposed to bombardment from cathode rays, when further considerable quantities of gas were evolved, quite sufficient to vitiate entirely experiments made at low pressures in the absence of this treatment. Readings on the McLeod gauge, with the trap C at room temperature, at - 78° C., and at the temperature of liquid air, showed that in the first few minutes these gases were a mixture of water vapour, a condensible gas, presumably carbon dioxide—and permanent gases. The following are typical figures obtained with the pyrex vessel for successive exposures, after baking out for 2 hours at about 500° C.

Table III.

Time of exposure (240 KV., 4.0 microamps.).	Volume of gas evolved uncondensable at - 78° C. (c.c. N.T.P.).
minutes.	per minute.
2	0.025
4	0.004
10	0.0029
10	0.0009

For a silvered pyrex vessel, the quantities were somewhat lower, viz. :—

Table IV.

Time of exposure (240 KV. 4.0 microamps.).	Volume of gas evolved uncondensable at - 78° C. (c.c. N.T.P.).
minutes.	per minute.
5	0.0035
5	0.0017
10	0.0007

It is interesting to note that the quantity of gas evolved in the first few minutes from the unsilvered surface corresponds approximately to a uni-molecular film on the surface of the glass. It was found, both in the silvered

and unsilvered vessels, that small quantities of permanent gas were evolved indefinitely, amounting to 0.0007 to 0.0009 c.c. per minute at 4.0 microamps and 240 KV., practically independent of the length of, or interval between, exposures. Thus bombardment with cathode rays is an extremely efficient method of outgassing a glass surface, 10 minutes' exposure being probably equivalent to several days of baking out and drying with phosphoric anhydride.

Ammonia, prepared by reducing the pressure over an aqueous solution, was passed over solid potash and phosphoric anhydride, and condensed in liquid air in the trap A. The permanent gases were pumped off and after removing the liquid air the first fraction was rejected and the next sublimed into the trap C, or, for experiments at low pressures, directly into the reaction vessel, in which case C, which was silvered, was cooled to -78° C. to remove mercury vapour. Before an exposure to the electron beam, the ammonia was tested for freedom from permanent gases. After exposure the undecomposed ammonia was frozen out in liquid air and the residual pressure noted, so giving the volume of permanent gases formed. They could be collected by means of the Töpler pump, measured directly, and, if required, analysed.

The following is a summary of the results obtained. Those in which the silvered vessel was used are denoted by "S," and the unsilvered by "P." Maximum voltage 240 KV.

Table V.

Pressure (cm. 18° C.).	Time (minutes).	Current (microamps.).	Volume of permanent gas formed.		Molecules of permanent gas per electron M/E.	$\frac{M}{E_p}$
			c.c. N.T.P.	c.c. per minute.		
P. 71.4	5	5.0	1.42	0.284	4080	57.1
P. 40.0	5	5.0	0.865	0.173	2484	32.1
P. 25.85	8	5.0	0.803	0.100	1442	55.8
P. 20.1	10	5.0	0.795	0.0795	1142	56.8
S. 20.05	10	3.25	0.543	0.0543	1199	59.8
P. 12.1	10	5.0	0.475	0.0475	682	56.4
S. 7.42	10	4.75	0.260	0.0260	393	53.0
P. 5.75	30	5.0	0.680	0.0227	325	56.5
P. 2.0	5	5.0	0.052	0.0104	149	74.5
S. 1.46	10	2.1	0.038	0.0038	130	89
S. 1.06	10	3.6	0.048	0.0048	96	90
S. 1.03	10	2.2	0.0298	0.0030	97	94
S. 0.82	10	3.5	0.037	0.0037	75.9	93
P. 0.279	10	5.0	0.0304	0.0030	43.6	156
S. 0.228	10	3.5	0.0130	0.0013	27	117
P. 0.113	10	5.0	0.0185	0.0018	26.5	235
S. 0.0570	10	4.0	0.0130	0.0013	23.3	409
P. 0.0200	30	5.0	0.0213	0.0011	14.7	735

The results show that over the range 71.4 to 5.75 cm. initial pressure, the rate of formation of permanent gas is approximately proportional to the pressure and independent of the nature of the surface (fig. 3).

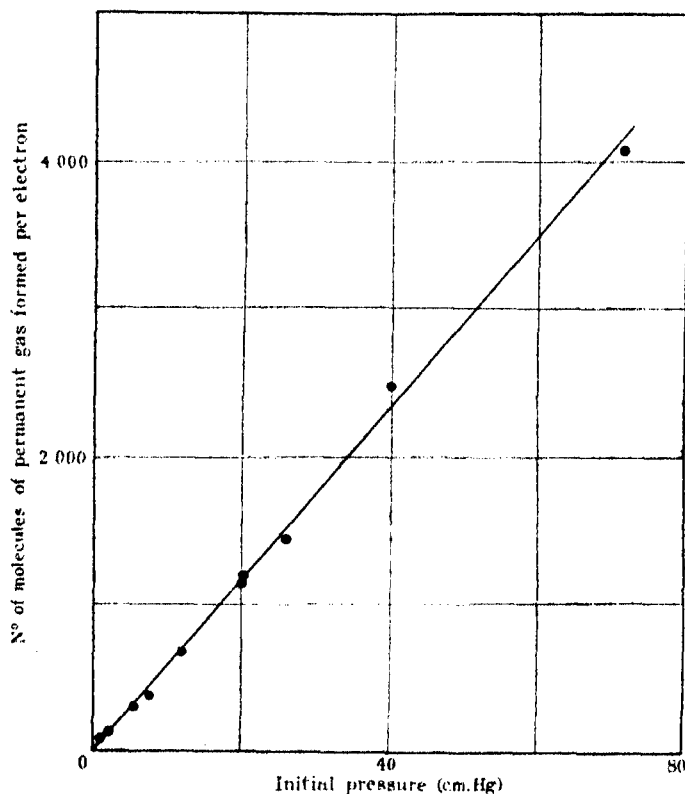


FIG. 3.

Analysis of the permanent gases was carried out by means of a small gas analysis apparatus of capacity 4.5 c.c., adapted from the type used by Norrish and Griffiths*, to whom we express our thanks. Analyses carried out with air, showed that results could be obtained correct to ± 0.005 c.c. The following results were obtained:—

Table IV.

Initial pressure.	Volume c.c. N.T.P.	Percentage hydrogen.	Percentage nitrogen.
cm.			
72.0	2.25	74.8	25.2
25.85	0.803	75.8	24.2
12.1	0.475	77.4	22.6
5.75	0.08	—	—

* 'J. Chem. Soc.,' p. 2829 (1928).

The excess of hydrogen in the samples obtained at low pressures suggested the formation of hydrazine. The ammonia in the next series of runs was, therefore, frozen out by liquid air, and after pumping off the greater part below the melting point, the remaining fraction was kept to test for hydrazine.

The test for hydrazine was carried out by a method which had been proved to be the most reliable and specific in detecting a small quantity. This depends on the thermal decomposition on a glass surface, which proceeds according to the equation



The fraction to be tested was cooled in carbon dioxide and ether in a side tube attached to the tap B; and the ammonia, which exerts a pressure of a few centimetres at this temperature, was pumped off. The tube was then heated for 5 minutes at about 400°C ., cooled again to -78°C ., and the pressure noted on the McLeod gauge; it was then cooled in liquid air and the pressure again noted. The permanent gases were pumped off and the liquid air again replaced by carbon dioxide. The first reading gives the total volume of ammonia and nitrogen, the second the nitrogen, and the third the ammonia. The following results were obtained:—

- (1) First reading over CO_2 and ether 0.041 mm.
- (2) First reading over liquid air 0.007 mm.
- (3) Second reading over CO_2 and ether 0.033 mm.

A separate test made with permanent gas showed that a correction factor of 1.125 was required in reading (2) to make it comparable with (1) and (3), which were obtained with the trap at a higher temperature. Hence the analysis gives the following relative volumes:—

	Pressure. mm.	Per cent.
Ammonia	0.033	80.5
Nitrogen	0.008	19.5
Total	0.041	100.0

The agreement with equation (1) is very good. The reliability of the method was proved by tests made with hydrazine from another source, the proportions being correct to 1 per cent. in each case.

A confirmatory test for hydrazine was made using the action on neutralised

* Askey, 'J. Amer. Chem. Soc.', vol. 52, p. 970 (1930).

gold chloride solution. A red coloration due to colloidal gold was obtained; careful blank experiments showed that no hydrazine was present in the original ammonia.

An attempt was made to determine the hydrazine directly by complete decomposition on a platinum filament. After thorough outgassing of the filament, the hydrazine, separated as described above from the excess of ammonia, was introduced, and the filament kept at a bright red heat until no condensible gas or vapour remained. The following result was obtained:—

Initial pressure—1.03 cm.

Exposure—10 minutes, 240 KV. maximum, 2.2 microamps.

Yield of permanent gas obtained directly—0.0298 c.c.

Yield of permanent gas by decomposition of hydrazine—0.0157 c.c.

It was found that the quantity of hydrazine obtained in two experiments at 180 KV. and at 75.0 and 66.3 cm. pressure respectively was too small to be separable from the large excess of ammonia. In the above results some of the hydrazine will have been lost, and the value of 0.0157 c.c. is probably somewhat low.

From the data obtained in the gas analyses and in the above experiment, we can make an approximate calculation of the fraction of decomposed ammonia converted into hydrazine. The results are as follows:—

Table VII.

Pressure	Yield (permanent gases).	$\frac{\text{Ammonia converted into } \text{N}_2\text{H}_4 + \text{H}_2}{\text{Total ammonia decomposed}} \times 100.$
cm.		
72.0	2.25	}
25.85	0.803	
12.1	0.475	
5.75	0.68	
1.03	0.0298	
		11
		30
		>30

An experiment was made to determine whether there is any evidence for the conclusion of McLennan and Greenwood that equilibrium is almost entirely on the side of ammonia formation at pressures of 4 mm., and slightly higher. The initial pressure was 10.6 mm., and the following results were obtained for successive exposures, the permanent gases not being pumped off between exposures.

Table VIII.

Exposure.	Current.	Yield.	M/E.
minutes.	microamps.	c.c. N.T.P.	
2	1.8	0.0040	80
5	1.8	0.0124	99
10	3.6	0.050	100

These results indicate that there is no tendency to approach equilibrium in the first 0.4 per cent. of decomposition.

The following results were obtained at 180 KV. maximum :—

Table IX.

Initial pressure.	Time.	Current.	Yield	$\frac{M}{E} \times 10^{-4}$.
cm.	minutes.	microamps.	c.c. N.T.P.	
75.0	10	0.50	0.230	3.30
75.0	10	1.31	0.654	3.58
66.3	10	1.31	0.603	3.30
58.3	10	1.31	0.597	3.27
				Mean 3.38

Here the yield is almost independent of the pressure.

The results obtained at low pressures must be corrected for the continuous evolution of permanent gas from the surface of the vessel. This correction amounts to approximately 14 molecules per electron *in vacuo*, and is possibly somewhat less at a pressure of 1 or 2 cm. When this correction is applied the following values of M/E and M/Ep are obtained.

Table X.

Pressure (cm.) . p.	M/E.	M/E (corrected).	M/Ep. (corrected).
P. 2.0	149	135	67.5
S. 1.46	130	116	79.5
S. 1.06	96	82	77.0
S. 1.03	97	83	81.0
S. 0.82	76	62	76.0
P. 0.279	43.6	29.6	106.0
S. 0.228	27	13	57.0
P. 0.113	26.5	12.5	111.0

In the last three results the relative correction is so large that not much reliance can be placed on the figures obtained, but we notice that over the range 0.82 to 2.0 cm. the corrected ratio M/Ep is consistently greater than that obtained at higher pressures. Thus, allowing for the increasing yield of hydrazine, at low pressures, we see that the rate of decomposition is not strictly proportional to the pressure over the whole range, but is relatively greater at low pressures.

Calorimetric Experiments.

Measurements of the total energy of the beam were made by a calorimetric method. The calorimeter was made of copper 0.1 mm. thick, the shape and dimensions in cms. being as shown in fig. 4. It was supported by silk threads

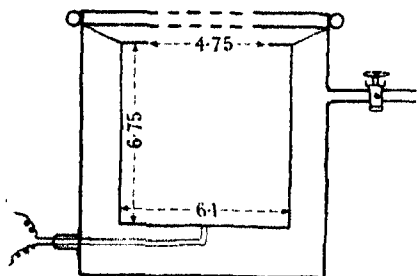


FIG. 4.

inside an outer vessel of thick copper, fitted with a water-cooled window support, bored to the same plan as that of the reaction vessel. The temperature was measured by means of iron-eureka thermocouples spot-welded to the surface of the copper and the current determined by means of a sensitive mirror galvanometer calibrated directly in degrees by varying the temperature

of the cold junction. The outer vessel was evacuated during experiments and kept in a water bath. Heating and cooling curves were taken and the amount of heat given to the calorimeter per second calculated, one of the leads being earthed. If the leads of the thermocouples were connected together and through a galvanometer to earth, the apparatus served as a Faraday cylinder, as the outer case was not in electrical connection with the calorimeter.

Sources of Error.—It is of great importance to make some estimate of the accuracy of the results obtained; the chief sources of error are therefore discussed in some detail:—

- (1) Radiation from the window. This source of error is greatly reduced by introducing a second water-cooled window between that of the cathode ray tube and the calorimeter, the space between the second window and the calorimeter being evacuated. The regularity of the heating curve, after correcting for radiation losses, indicates that this error is small.

- (2) Incomplete absorption of energy. The error due to some of the energy being lost owing to reflection of electrons out of the calorimeter is reduced as far as possible by the shape of the calorimeter. It is to be noted that these two errors will be to some extent mutually compensating.
- (3) Non-uniformity of temperature over the surface of the calorimeter. It is possible that the temperature was lower near the top of the vessel, where fewer electrons strike directly, than at the base. To reduce this source of error a number of thermocouples were welded to various parts of the calorimeter and connected in parallel. Further, measurements were made with a single thermocouple fixed just below the lip, near the silk support, and showed that the temperature at this point was not more than 15 per cent. lower than that measured by the couples in parallel.
- (4) Other possible errors. The method reproduces accurately the conditions of the chemical experiments. It differs from that of Busse and Daniells, who used no second window but an air space of 2 cm., which they calculated corresponded to the window used. Cooling accurately obeyed Newton's law throughout the temperature ranges employed (about 4° C.), and the correction could be accurately applied. Variations in current and maximum voltage on the discharge tube would be similar to those in the chemical experiments and were shown to be small by the reproducibility of results. The leads were of fine iron and eureka wire and their weight small compared with that of the copper vessel.

The variability of results in the calorimetric and chemical experiments indicate a possible error not greater than ± 5 per cent. The magnitude and sign of the systematic errors discussed in (1), (2) and (3) above is more difficult to estimate, but we consider that our results are certainly correct to ± 20 per cent. and are probably of a higher order of accuracy.

The following results were obtained :—

Table XI.

KV. (maximum).	Current (microamps.).	Rate or rise of temperature (corrected) degrees per minute.	Rate of supply of energy (watts).	Mean energy per electron.
240	3.90	4.285	} 0.489	KV. 125
240	3.90	4.30		
180	1.31	0.57	} 0.629	48
	1.31	0.52		
	1.31	0.57		

Discussion of Results.

We must consider how our results fit in with the theory that reaction is due to ionisation, a definite number of molecules reacting per ion pair produced. At low pressures, at which the majority of electrons reach the walls without an appreciable diminution in their energy, the amount of ionisation produced would be proportional to the number of molecules per cubic centimetre, that is, to the pressure, if that produced by secondary electrons and reflected electrons can be ignored. On the other hand, if the vessel were sufficiently large or the pressure sufficiently high to ensure that no electrons reached the walls with an appreciable fraction of their initial energy, then the amount of ionisation produced should be independent of the pressure. Calorimetric experiments made under these conditions should give a true value of the number of electron-volts per molecule reacting. The results obtained at 180 KV. maximum show that the yield is practically independent of the pressure, and hence should give the true value required. In the intermediate case we have two effects to consider. First, as the pressure is raised an increasing fraction of the electrons lose all their energy before reaching the walls, and, secondly, the amount of ionisation per unit length of path increases as the velocity of the electrons decreases. As we do not know the distribution of velocities in the electron beam, it is impossible to calculate a relation between ionisation and pressure over this range.

Our results indicate that the rate of reaction is approximately proportional to the pressure over a considerable range of pressures, the relative rate increasing somewhat at low pressures. It is not unreasonable to suppose that the amount of ionisation produced is approximately proportional to the pressure until a considerable fraction of the electrons fail to reach the walls, and hence that a definite amount of decomposition occurs for each ion pair formed. The

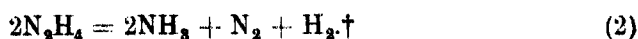
increase in the relative rate at low pressures is probably due to the effect of secondary electrons, or possibly to decomposition in an absorbed film, though we have no evidence from a comparison of the yields in glass and silvered vessels that the nature of the surface affects the yields. Since the approximate linear law holds up to the highest pressure employed at 240 KV. maximum, it is clear that many of the electrons reach the walls still possessing a certain amount of energy. This is what would be expected with a vessel of the dimensions employed and electrons of average energy 124 KV. entering the vessel. Hence values of the number of electron-volts per molecule reacting, will be considerably too high if calculated from our results at 240 KV.

As no data on the ionisation of ammonia by cathode rays are available we can only calculate the value of M/N if we make the arbitrary, but perhaps reasonable, assumption that the amount of energy required to produce one ion pair in ammonia relative to air, is the same for cathode rays as for α -particles. Taking 0.95* as the total ionisation for ammonia relative to that for air, the following values are obtained.

Table XII.

Maximum voltage. KV.	Mean energy per electron. KV.	Molecules decomposed per electron.	Electron volts per molecule.	M/N.
240	125	2040	61	> 0.56
180	48	1690	28.4	1.19

In calculating these results the hydrazine has been ignored. In view of the results of the analyses, it is reasonably certain that the fraction of the decomposed ammonia converted into hydrazine in the experiments at 180 KV. is less than 20 per cent., which means that the value of 1.19 is not low on this account by more than 10 per cent. since hydrazine is probably decomposed, as in the photochemical reaction, according to the equation



Wourtsel calculated from his results $M/N = 0.8$, but this value is probably low owing to the deposition of the radioactive deposit on the walls of the containing vessel during the experiment. If we assume that all the radio-

* The value taken by Wourtsel for his calculations. Laby [*Proc. Roy. Soc., A*, vol. 79, p. 206 (1907)] gives 0.90.

† Elgin and Taylor, *J. Amer. Chem. Soc.*, vol. 51, p. 2059 (1929).

active deposit reaches the walls, we obtain $M/N = 1.24$. Thus agreement between the results is satisfactory.

The formation of hydrazine is an interesting and important point. Our results show that it is formed in relatively larger quantities, even for greater relative yields, at low pressures. If hydrazine is an intermediate product it is clear that it must be decomposed much faster than ammonia. Two possible hypotheses may explain this and both agree with the relatively larger yields at low pressures.

- (a) Hydrazine may be decomposed by a chain reaction, the chains being broken by the walls, and therefore longer in presence of a large excess of ammonia.
- (b) Hydrazine molecules may be formed in the excited state, and, if deactivated by radiation before collision, normal hydrazine results, but if not, further decomposition takes place. In this case the yield of hydrazine will be greater the longer the mean time between two collisions, that is, the lower the pressure. A decision cannot be made without further experiment.

The mean energy per ion pair (taken as 35 electron-volts) is considerably higher than the first ionisation potential (11.1 volts).^{*} A considerable part of the energy is accounted for by secondary electrons left with energies too small to cause ionisation, but in addition there is probably a certain amount of excitation and possibly a few multicharged ions may be formed. The greater part of the chemical reaction is probably due, however, to simple ionisation.

There are two possibilities, (a) the combination of a positive ion and an electron, and (b) the combination of a positive and a negative ion. The first process cannot occur unless there is some means of removing the excess energy, such as three-body collision with another molecule or with the walls, or dissociation into simpler molecules, it being well known that loss by radiation is difficult. In this case the reaction would be



This is preferred to the alternative mechanism

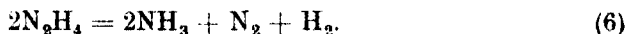


^{*} Mackay, 'Phil. Mag.', vol. 46, p. 828 (1923); Bartlett, 'Phys. Rev.', vol. 33, p. 169 (1928).

The existence of NH has been proved by observation of band spectra* and it may be the active gas observed by Lavin and Bates.† This would be followed by



and finally

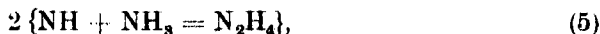
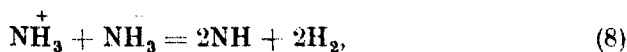


On account of the rarity of simple recombinations of the type

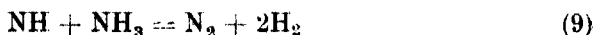


this mechanism requires $M/N = 1$.

Wourtsel (*loc. cit.*) found, however, that M/N rises to 2.55 at 318° C. or 4.0 if corrected for the radioactive deposit, an observation paralleled in the case of the photochemical reaction, in which a quantum efficiency of 3.3 was observed at 500° C.‡ It is impossible to account for such a high efficiency by mechanism (a), and (b) is therefore to be preferred. Its relative importance depends on the probability of reaction (b), and in spite of the relatively low electron affinity of ammonia§ it is quite possible that it plays the most important part. In this case, unlike (a), recombination may occur without chemical reaction. The mechanism



therefore allows a *maximum* efficiency of two molecules of ammonia decomposed per ion pair. If at high temperatures



is favoured in place of (5) we can account for a maximum efficiency of 4.

Comparison of the Results obtained in the Decomposition of Ammonia by Cathode Rays with those obtained with other Radiations.—We have shown that our results agree quantitatively with those obtained by Wourtsel for α -particles. A comparison with the photochemical reaction is therefore of interest and some information should be obtainable regarding the similarity or difference between photochemical reactions and reactions due to ionisation. Lind in several

* Hulthén and Nakamura, 'Nature,' vol. 119, p. 235 (1927).

† 'Nature,' vol. 125, p. 709 (1930).

‡ Kuhn, 'C. R.,' vol. 178, p. 708 (1924).

§ Attachment constant 9.9×10^4 . Wahlin, 'Phys. Rev.,' vol. 19, p. 173 (1922).

recent papers* has demonstrated similarity in the two cases, and the summaries in his book (p. 211), and in Griffith and McKeown's "Photo Processes in Gaseous and Liquid Systems"† (pp. 671-73), show that quantum efficiency is generally of the same order of magnitude, though not necessarily equal to the M/N ratio.

Kuhn using radiation between the limits $\lambda = 202.5 \mu\mu$ and $214.0 \mu\mu$, found between 10° and 20° C. a quantum efficiency of 0.4 to 0.5 independent of pressure between 900 mm. and 5 mm., reaction proceeding smoothly to completion at a speed proportional to the rate of absorption of energy. He did not test for hydrazine in the initial stages of decomposition. Kassel and Noyes‡ using radiation of the range $\lambda = 160$ to $190 \mu\mu$ found $M/h\nu = 0.7$. It appears therefore that in this case $M/h\nu$ is somewhat less than M/N at ordinary temperatures and increases with decreasing wave-length.

Dickinson and Mitchell,§ and Bates and Taylor|| investigated both the direct and mercury sensitised reactions. Analyses of the decomposition products by Bates and Taylor, who used a flow method, showed excess of hydrogen thus:—

Sensitised reaction	H ₂ 89 per cent., N ₂ 11 per cent.
Direct reaction	H ₂ 96 per cent., N ₂ 4 per cent.

Although they suggested that this might be due to hydrazine formation, they did not detect it directly. In view of our results there is every reason to believe that hydrazine formation was the explanation. In view of these results and the similar effect of temperature in the photochemical and ionic reactions, it seems probable that a similar mechanism accounts for the two cases.

Bredig, Koenig and Wagner¶ using the silent discharge obtained large yields of hydrazine by a flow method. The highest yields, up to 80 per cent. of the decomposed ammonia, were obtained at relatively low pressures with a high rate of flow, a result strictly in agreement with our own.

We have obtained no support for the conclusions of McLennan and Greenwood that at 4 mm. pressure equilibrium was entirely on the side of formation and that the initial rate of decomposition is independent of pressure. They followed the reaction by pressure changes only, and made no analysis of the

* *Inter alia*, 'J. Phys. Chem.,' vol. 32, p. 573 (1928).

† Longmans (1929).

‡ 'J. Amer. Chem. Soc.,' vol. 49, p. 2495 (1927).

§ 'Proc. Nat. Acad. Sci.,' vol. 12, p. 692 (1926).

|| 'Proc. Nat. Acad. Sci.,' vol. 12, p. 714 (1926); 'J. Amer. Chem. Soc.,' vol. 49, p. 2438 (1927).

¶ 'Z. Phys. Chem.,' A, vol. 139, p. 211 (1928); vol. 144, p. 213 (1929).

products. We can see from our results that at low initial pressures the change does not give a measure of the amount of decomposition for the following reasons :—

- (1) The reaction $2\text{NH}_3 = \text{N}_2\text{H}_4 + \text{H}_2$ proceeds without change of pressure.
- (2) The rise in pressure at low initial pressures may be due to decomposition or desorption of a surface absorbed film.
- (3) Even *in vacuo* there is a small evolution of gas from the surface.

It is to be noted that the relative pressure changes at 4 mm. would be small in the first few minutes of reaction if the current entering the reaction vessel is of the same order of magnitude as in our experiments, even if decomposition proceeded directly as they supposed.

Experiments on the synthesis of ammonia are in progress and we have found that the rate of formation of ammonia is small compared with its decomposition over a considerable range of pressures. It was found by McLennan and Greenwood that the first few results with a vessel that had been exposed to air for some time were irregular. They ascribed this to the surface in its original state possessing the property of decomposing ammonia under the influence of cathode rays, a property destroyed by prolonged exposure to ammonia, nitrogen or hydrogen. In view of our observation that considerable quantities of gas are evolved from the surface of a vessel which has been exposed to air, even after thorough baking out, it would appear that the pressure increases observed were due to the same cause.

We may conclude that the cathode ray method of investigation is capable of giving quantitative results, and possesses great advantages over the α -particle method for the examination of the initial stages of the reaction. Our accuracy is limited by the type of transformer used, but there is reason to believe that this method will give, when ionisation data are available, values for the M/N ratio of the same order of accuracy as those obtained with α -particles, or the M/h ν ratios obtained in photochemical reactions. The method, on the other hand, is not suitable for work at low pressures, owing to the complications produced by the intense bombardment of the glass.

Summary.

1. Ammonia is decomposed by cathode rays into hydrazine, nitrogen and hydrogen, the relative yield of hydrazine for the same relative amount of decomposition, being greater at low pressures.
2. A calorimeter has been designed for the measurement of the energy of

the electrons entering the reaction vessel, capable of giving results for the amount of energy per molecule reacting, of the same order of accuracy as can be obtained when using α -particles.

3. Good agreement is obtained with Wourtsel's results for α -particles in the same reaction. The results agree qualitatively with those obtained in the silent discharge and in ultra-violet light. It is calculated that 1.2 molecules of ammonia are decomposed for each ion pair formed.

4. We conclude that the cathode ray method of investigation possesses advantages for both qualitative and quantitative work, at normal and moderate pressures, and especially for the examination of the initial stages of the reaction.

Acknowledgments.

Our best thanks are due to Prof. E. K. Rideal, F.R.S., for suggesting the problem and for his constant advice and encouragement, and to Sir Ernest Rutherford, in whose laboratory the cathode-ray tube was installed. Also to the Goldsmiths' Company for a Senior Studentship granted to one of us (G. R. G.), and to the Royal Commissioners to the Exhibition of 1851 for a Senior Studentship granted to the other (T. E. A.), also to the Imperial Chemical Industries for assistance in defraying part of the cost of the chemical apparatus, and to the Metropolitan-Vickers Electrical Co. for the gift to the Cavendish Laboratory of the Tesla transformer.

The Chemical Constant of Hydrogen Vapour and the Entropy of Crystalline Hydrogen.

By T. E. STERN, B.Sc., Trinity College, Cambridge.

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Introduction.

In a paper called "The Chemical Constant of Hydrogen Vapour and the failure of Nernst's Heat Theorem,"* R. H. Fowler has investigated the vapour pressure of hydrogen crystals at low temperatures; taking account of the existence of two sorts of hydrogen molecules, namely, ortho-hydrogen with even rotational quantum numbers and para-hydrogen with odd rotational quantum numbers, which retain their individuality over long periods at very low temperatures. By the use of the classical statistics, he was able to show that at very low temperatures hydrogen, as obtained by cooling hydrogen gas from ordinary temperatures, ought to have very nearly the experimentally observed chemical constant. Since the theory of the specific heat of hydrogen yielded correct values at low temperatures, it followed that at ordinary temperatures also his theory would yield a correct value for the chemical constant. Finally, from the form of the partition function for hydrogen gas, Fowler attempted to obtain inferences concerning the validity of Nernst's heat theorem.

By the use of the classical statistics fairly accurate results were obtained. But we shall find that when we make use of the Einstein-Bose statistics—the correct statistics for an assembly of hydrogen molecules—a result will be obtained for the vapour pressure of hydrogen crystals at low temperatures which will furnish a value for the chemical constant of hydrogen in even closer agreement with experiment than Fowler's result. Further, as the result of the Einstein-Bose statistics, slight variations will be found to occur in the composition of a mixed crystal of the two sorts of hydrogen as it is allowed to build up at low temperatures, from the gas. We shall then follow the vapour pressure equation, which is correct at low temperatures through to ordinary temperatures, and show how a term $\frac{1}{2} \log 3$ appears in the chemical constant when we calculate its value at ordinary temperatures—a thing not obvious without explicit calculation. We shall investigate the effect upon equilibria involving the

* R. H. Fowler, 'Proc. Roy. Soc.,' A, vol. 118, p. 52 (1928).

gaseous and crystal forms of hydrogen of a change, if any change occurs, in the moment of inertia of a hydrogen molecule when it condenses from the gas on to a crystal. And finally, while leaving the position of Nernst's theorem itself for discussion in another paper, we shall calculate by statistical mechanics the difference between the entropies of the different sorts of crystalline hydrogen at the absolute zero of temperature.

§ 1. *The Statistical Mechanics of Assemblies containing Hydrogen Gas and Mixed Crystals of Para- and Ortho-hydrogen.*

We consider an assembly containing X molecules of para-hydrogen, and X' molecules of ortho-hydrogen, between which it is assumed that no interchanges occur. A molecule of the former type can be represented by only $2j + 1$ linearly independent wave-functions where j is the rotational quantum number; corresponding to the $2j + 1$ possible eigenvalues of the z component of rotational angular momentum. A molecule of the latter type, however, can be represented by any one of $3(2j + 1)$ linearly independent wave-functions; corresponding to the $2j + 1$ possible eigenvalues of the z component of rotational angular momentum and the three possible eigenvalues of the z component of nuclear spin angular momentum. The observables involved commute with each other so that we may assign these eigenvalues independently. The wave-function of an assembly of hydrogen molecules must be symmetrical in all of the molecules. We are interested in the total number of linearly independent wave-functions of this type capable of describing the assembly when the total energy of the assembly is E .

Let N be the number of molecules of para-hydrogen in the gas and let N' be the number of molecules of ortho-hydrogen in the gas. Let P and P' be the numbers of molecules of the two sorts in the crystalline phase. We suppose that the partition function for the normal modes of vibration of a mixed crystal containing in all L molecules of both sorts of hydrogen is of the form $\kappa(z)^L$; and that the rotational partition functions for the molecules, both in the crystal and in the gas (we defer until later a discussion of this assumption) are for the para-hydrogen

$$(1) \quad f(z) = \sum_{j=0,2,4,\dots}^{\infty} (2j+1) z^{j(j+1)},$$

and for the ortho-hydrogen

$$f'(z) = \sum_{j=1,3,5,\dots}^{\infty} 3(2j+1) z^{j(j+1)},$$

where $\varepsilon = h^2/(8\pi^2 A)$, h being Planck's constant, and A being the moment of inertia of the molecule. The normal modes of vibration of the crystal contribute to the total number of possible linearly independent wave-functions capable of describing the entire assembly a factor equal to the coefficient of z^Q in $\kappa(z)^{P+P'}$, when the total energy of the normal modes of vibration of the crystal is Q .

We must now obtain an expression for the factor, contributed to the total number of linearly independent wave-functions capable of representing the assembly, by the molecular rotations. Consider first, for simplicity, a "crystal" composed of three similar molecules arranged in any manner among the lattice points a , b and c . Two of the molecules are to have rotational wave-functions of class A , the other of class B . There is only one independent wave-function A of class A , but class B has two linearly independent wave-functions B^1 and B^2 . Then the possible wave-functions for this crystal, symmetrical in all the molecules and linearly independent, if we neglect oscillations, are to a first approximation the permanents

$$\begin{vmatrix} A_a(1) & A_a(2) & A_a(3) \\ A_b(1) & A_b(2) & A_b(3) \\ B_c^1(1) & B_c^1(2) & B_c^1(3) \end{vmatrix}, \quad \begin{vmatrix} A_a(1) \\ A_b(1) \\ B_c^2(1) \end{vmatrix}, \quad \begin{vmatrix} A_a(1) \\ B_b^1(1) \\ A_c(1) \end{vmatrix},$$

$$\begin{vmatrix} A_a(1) \\ B_b^2(1) \\ A_c(1) \end{vmatrix}, \quad \begin{vmatrix} B_a^1(1) \\ A_b(1) \\ A_c(1) \end{vmatrix}, \quad \begin{vmatrix} B_a^2(1) \\ A_b(1) \\ A_c(1) \end{vmatrix};$$

where, for instance, $B_c^1(2)$ means the first rotational wave-function of class B for the second molecule, associated with the lattice point c . We have written down only the first columns of the permanents denoting the last five wave-functions. We observe that these wave-functions are $1^2 2^1 3!/1! 2! = 6$ in number.

We see from this example that the molecular rotations in the crystal contribute to the total number of possible wave-functions of the entire assembly, a factor equal to the coefficient of z^S in

$$f(z)^P f'(z)^{P'} (P + P')! / P! P'!$$

when the total energy of molecular rotation in the crystal is S . Thus the crystal, when its energy is U , contributes to the total number of wave-functions of the assembly a factor equal to the coefficient of z^U in

$$f(z)^P f'(z)^{P'} \kappa(z)^{P+P'} (P + P')! / P! P'!$$

or equal to the coefficient of $x^P x'^{P'} z^U$ in

$$1/\{1 - (xf(z) + x'f'(z)) \kappa(z)\}.$$

The vapour, if its energy is F , contributes to the total number of wave-functions a factor equal to the coefficient of $x^N x'^{N'} z^F$ in

$$\Pi \left(\frac{1}{1 - xz^*} \right) \Pi \left(\frac{1}{1 - x'z'^*} \right),$$

where the Π 's are taken over all the energy values; the primed and unprimed letters referring as before to ortho-hydrogen and para-hydrogen. Hence the total number of linearly independent wave-functions, symmetric in the molecules, capable of representing the entire assembly of energy E and corresponding to all possible distributions of the molecules between the phases, is the coefficient of $x^X x'^{X'} z^E$ in

$$\frac{\Pi \left(\frac{1}{1 - xz^*} \right) \Pi \left(\frac{1}{1 - x'z'^*} \right)}{1 - (xf(z) + x'f'(z)) \kappa(z)}.$$

Hence this number

$$C = \left(\frac{1}{2\pi i} \right)^3 \iiint \frac{dx dx' dz \Pi \left(\frac{1}{1 - xz^*} \right) \Pi \left(\frac{1}{1 - x'z'^*} \right)}{x^{X+1} x'^{X'+1} z^{E+1} \{1 - (xf(z) + x'f'(z)) \kappa(z)\}}.$$

By the usual arguments* we find for the mean values

$$(2) \quad \bar{P} = \frac{\xi f(\theta) \kappa(\theta)}{1 - (\xi f(\theta) + \xi' f'(\theta)) \kappa(\theta)},$$

$$(2') \quad \bar{P}' = \frac{\xi' f'(\theta) \kappa(\theta)}{1 - (\xi f(\theta) + \xi' f'(\theta)) \kappa(\theta)},$$

$$(3) \quad \bar{N} = -\xi \frac{\partial}{\partial \xi} \Sigma \log(1 - \xi \theta^*),$$

$$(3') \quad \bar{N}' = -\xi' \frac{\partial}{\partial \xi'} \Sigma \log(1 - \xi' \theta'^*).$$

Here the parameters ξ , ξ' and θ ($= e^{-1/kT}$), corresponding to the partial potentials and to the temperature, are determined by the unique position of the saddle-point of the integrand of C , given by the vanishing of its three partial differential coefficients. We have in addition

$$\bar{N} + \bar{P} = X \quad \bar{N}' + \bar{P}' = X$$

$$X' = 3X.$$

* R. H. Fowler, "Statistical Mechanics," chapters 5 and 21.

If $\bar{P} + \bar{P}'$ denoting the number of molecules in the crystal is large, then from (2) and (2')

$$(4) \quad (\xi f(\theta) + \xi' f'(\theta)) \kappa(\theta) = 1 - O(1/(\bar{P} + \bar{P}')).$$

We have defined $\kappa(\theta)$ so that $\kappa(0) = 1$ and therefore $\kappa(\theta) \gg 1$. It follows from the discussion of R. H. Fowler* that we may replace the expression (3) for $\bar{N}$ by

$$(5) \quad \bar{N} = \xi \frac{\partial}{\partial \xi} \frac{(2\pi mkT)^{3/2} V}{h^3} \sum_{n=1}^{\infty} \frac{\xi^n}{n^{5/2}} \sum_{j=0, 2, 4, \dots}^{\infty} (2j+1) e^{-nj(j+1)/kT}$$

where m is the mass of a molecule of hydrogen and k is Boltzmann's constant; since it follows from (4) that $\xi < 1$. Further, although ξ' in expression (3') is enormously greater than unity, it follows from (4) that $\xi'\theta'$ is always less than unity; so that the expansion of the logarithms in series, and the subsequent use of Fowler's discussion, is valid in this case also. Hence,

$$(5') \quad \bar{N}' = \xi' \frac{\partial}{\partial \xi'} \frac{(2\pi mkT)^{3/2} V}{h^3} \sum_{n=1}^{\infty} \frac{\xi'^n}{n^{5/2}} \sum_{j=1, 3, 5, \dots}^{\infty} 3(2j+1) e^{-nj(j+1)/kT}.$$

§ 2. The Composition of a Mixed Crystal of Ortho- and Para-hydrogen.

We now let $\bar{P}' = s\bar{P}$. Then, from (2), (2'), and (4)

$$\xi f(\theta) = 1/(s+1) \kappa(\theta); \quad \xi' f'(\theta) = s/(s+1) \kappa(\theta);$$

and from the relations of the last section

$$s - 3 = \frac{1}{X} (s\bar{N} - \bar{N}').$$

When T is small we thus find, using (5) and (5') and neglecting trivial terms, that

$$(6) \quad s = 3 + \frac{4}{X + X'} \frac{G(T)}{K(T)} \sum_{n=2}^{\infty} \frac{s - s^n/9^{n-1}}{(s+1)^n K(T)^{n-1} n^{3/2}},$$

where $G(T) = (2\pi mkT)^{3/2} V/h^3$, the partition function for translatory motion in the gas. Using Newton's method of successive approximations, we find that

$$(7) \quad s = 3 + \frac{1}{X + X'} \frac{G(T)}{K(T)} \left(\frac{0.177}{K(T)} + \frac{0.032}{K(T)^2} + \dots \right) \\ + \left(\frac{G(T)}{(X + X') K(T)} \right)^2 \left(\frac{0.01}{K(T)^3} + \dots \right) + \dots,$$

which should be correct to about the nearest 0.02.

* R. H. Fowler, *loc. cit.*, pp. 535, 536.

Considering hydrogen at very low temperatures, we shall assume the result from the following section that $\bar{N} + \bar{N}' = G(T)/K(T)$ nearly; and thus we find, nearly,

$$s = 3 + 0.177 \frac{\bar{N} + \bar{N}'}{X + X'} \frac{1}{K(T)} + \dots$$

The value of the partition function for the crystal, $K(T)$, may be obtained from thermal data. Thus for hydrogen at 17° K. it is approximately 1.23. As we condense hydrogen gas at constant temperature to the crystalline form, the crystal starts by being composed of the two sorts of molecules roughly in the ratio of $3 + 0.177/K(T)$ to 1; and as the crystal builds up, the ratio approaches 3:1. At 17° K, for example, the ratio should at first be nearly $3\frac{1}{2}:1$; and if the experiment is performed at temperatures very near the absolute zero the ratio, when the crystal is small, may be as great as $3\frac{1}{2}:1$. At higher temperatures, the ratio is always nearly 3:1.

It should be observed that this effect is due simply to the Einstein-Bose statistics obeyed by the molecules. In another section we shall discuss possible variations in the constitution of mixed crystals of hydrogen caused quite differently.

§ 3. *The Chemical Constant of Hydrogen Vapour at Low Temperatures.*

We use in this section the value $s = 3$; the reader can readily verify that even if we used the greatest value $s = 3\frac{1}{2}$ arrived at in the preceding section, the changes in the following analysis would be trivial. From (5) and (5') it follows, with sufficient accuracy when T is small, that

$$(8) \quad \bar{N} + \bar{N}' = \frac{G(T)}{K(T)} \sum_{n=1}^{\infty} \frac{1 + 3^n/9^{n-1}}{4^n K(T)^{n-1} n^{3/2}}.$$

For hydrogen at 17° K. (the mid-point of Eucken's range at low temperatures*), we find that

$$(9) \quad \bar{N} + \bar{N}' = 1.04 G(T)/K(T)$$

nearly. The factor 1.04 was lost by Fowler when he used classical statistics.

The chemical constant of a substance is defined as the constant i in the equation

$$(10) \quad \log_{10} p = -\frac{M\lambda_p}{RT} + \frac{(C_p)_0}{R} \log_{10} T + M \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} \{(C_p)_1 - C_{sol}\} dT'' + i,$$

* Eucken, 'Z. Physik,' vol. 29, p. 1 (1924).

connecting the vapour pressure, p , of a crystalline substance with the absolute temperature, T ; the gas constant, R ; the work required to evaporate one gram molecule at the absolute zero, λ_0 ; the constant part $(C_p)_0$, of the specific heat per gram molecule of the gas at constant pressure; the variable part, $(C_p)_1$; and the specific heat at constant pressure of the solid phase, C_{sol} , per gram molecule. $M = \log_{10} e$. It is usual to measure p in atmospheres (1.013×10^6 dynes/cm.²). Experiments are usually conducted over a certain limited range of temperatures to determine λ_0 and i ; and the experimenters (e.g., Eucken) assume some value for $(C_p)_0$ which corresponds to the constant part of the specific heat of the gas for this range. $(C_p)_0$ thus depends upon the temperature range, and different values of the chemical constant i will result from the use of different values for $(C_p)_0$.

For hydrogen at low temperatures $(C_p)_0 = 5R/2$, and $(C_p)_1 = 0$. By comparing (9) with (10) in the fashion pursued by R. H. Fowler in a similar case,* we find for the chemical constant of hydrogen vapour at low temperatures the value

$$i = -1.11.$$

This is algebraically larger by 0.02 than the value obtained by the use of the classical statistics, and is in excellent agreement with Eucken's experimental value

$$i = -1.09 \pm 0.02.$$

§ 4. The Chemical Constant of Hydrogen Vapour at Ordinary Temperatures.

At ordinary temperatures we may consider that $(C_p)_0$ in (10) is equal to $7R/2$, and that $(C_p)_1$ is again 0. At ordinary temperatures the "rotational" term in the specific heat of hydrogen has contributed practically its maximum value R to the specific heat, and vibrational terms are as yet unimportant. It is instructive and interesting to follow through by statistical mechanics the change from low to ordinary temperatures, when we employ equation (10) with these new values; and to calculate what the chemical constant of hydrogen vapour must then be.

We can certainly use equation (10) at ordinary temperatures, provided that we use $(C_p)_0 = 5R/2$ and our old value of i , but now it will be necessary to assign to $(C_p)_1$ its correct value equal to the rotational specific heat of hydrogen.

* R. H. Fowler, *loc. cit.*, pp. 144, 145.

Let T_1 be a temperature above which we may suppose the rotational specific heat to be R , and let $T_1 \leq T$. Then the integral

$$\begin{aligned}
 (11) \quad & \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_1 dT'' \\
 &= \int_0^{T_1} \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_1 dT'' + \int_{T_1}^T \frac{dT'}{RT'^2} \left(\int_0^{T_1} (C_p)_1 dT'' + \int_{T_1}^{T'} R dT'' \right) \\
 &= \int_0^{T_1} \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_1 dT'' + \log T - \log T_1 + \frac{\Delta E_r}{RT} - \frac{\Delta E_r}{RT_1},
 \end{aligned}$$

where we have set

$$\Delta E_r = RT_1 - \int_0^{T_1} (C_p)_1 dT''.$$

We seek the quantity i' in the equation, correct at ordinary temperatures,

$$(12) \quad \log_{10} p = -\frac{M\lambda_0'}{RT} + \frac{5}{2} \log_{10} T - M \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_{rot})_1 dT'' + i'.$$

By inspection of equations (10), (11), and (12), it follows that $\lambda_0' = \lambda_0 - \Delta E_r$, and that $i' = i + Mi_r$, where

$$i_r = \int_0^{T_1} \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_1 dT'' - \log T_1 - \frac{\Delta E_r}{RT_1}.$$

It is obvious from physical considerations that this must be independent of T_1 if T_1 is sufficiently large. We may neglect the third term since this approaches zero as T_1 increases indefinitely. The first term is

$$J = \int_0^{T_1} \frac{dT'}{RT'^2} \left[N\theta \frac{\partial}{\partial \theta} \log r(\theta) \right]_0^{T'}$$

where N is Avogadro's number and $r(\theta)$ is the rotational partition function. But*

$$(13) \quad \log r(\theta) = \frac{3}{4} \log f'(\theta) + \frac{1}{4} \log f(\theta).$$

We can therefore deduce, using (1), that the integrand of J is

$$\frac{1}{RT'^2} \left(RT'^2 \frac{\partial}{\partial T'} \log R(T') - \frac{3}{4} \pi N \right).$$

* Fowler, *loc. cit.*, p. 57.

It will now be observed that the integrals of the separate terms diverge at the lower limit so that they must not be separated. We consider therefore

$$\begin{aligned} J &= \lim_{\lambda \rightarrow 0} \int_{\lambda}^{T_1} \partial T' \left(\frac{\partial}{\partial T'} \log R(T') - \frac{3\varepsilon}{2kT'^2} \right) \\ &= \log R(T_1) + \frac{3\varepsilon}{2kT_1} - \lim_{\lambda \rightarrow 0} \left(\log R(\lambda) + \frac{3\varepsilon}{2k\lambda} \right). \end{aligned}$$

From (1) the last term

$$\begin{aligned} &= \lim_{\lambda \rightarrow 0} \left(\frac{3}{4} \log 9 - O(\exp - 6\varepsilon/k\lambda) \right) \\ &= \frac{3}{4} \log 9. \end{aligned}$$

Since we may neglect the second term in J which approaches zero as T_1 increases, we have very nearly

$$i_r = \log \frac{R(T_1)}{T_1} - \frac{3}{4} \log 9.$$

From (1) and (13)

$$\begin{aligned} \log \frac{R(T_1)}{T_1} &= \frac{3}{4} \log 3 - \sum_{j=1,3,5,\dots}^{\infty} (2j+1) e^{-j(j+1)\varepsilon kT_1} \\ &\quad + \frac{1}{4} \log \sum_{j=0,2,4,\dots}^{\infty} (2j+1) e^{-j(j+1)\varepsilon kT_1} - \log T_1 \\ &= \frac{3}{4} \log \frac{3kT_1}{2\varepsilon} + \frac{1}{4} \log \frac{kT_1}{2\varepsilon} - \log T_1 \end{aligned}$$

very nearly. Therefore

$$\log \frac{R(T_1)}{T_1} = \log \frac{k}{\varepsilon} + \frac{3}{4} \log 3 - \log 2,$$

and

$$i_r = \log \frac{8\pi^2 A k}{h^2} - \frac{3}{4} \log 3 - \log 2.$$

Taking $\log_{10} A = -40.33$, the optical value, we find that

$$M i_r = -2.59.$$

Eucken,* from empirical data, obtains the value -2.595 . This agreement is excellent, and is in fact a check on the specific heat theory for hydrogen at low and ordinary temperatures. Thus for our chemical constant of hydrogen vapour at ordinary temperatures we obtain the value

$$i' = -3.70,$$

in excellent agreement with Eucken's value -3.68 ± 0.03 .

* Eucken, *loc. cit.*

§ 5. *The Effects upon Equilibria of Possible Differences between the Moments of Inertia of Hydrogen Molecules in the Gas and in Crystals.*

Along with Mr. R. H. Fowler, we have assumed in the above discussion that the molecules in the crystal possess the same rotational partition functions that they have in the gas. Now they can have the same partition functions only if they have the same energy levels; and they can have the same energy levels only if they can rotate freely in the crystal, and also possess the same moment of inertia that they have in the gas. It is by no means obvious *a priori* that molecules in general are able to rotate in crystals. It appears from recent theoretical investigations* that in some crystals molecules cannot rotate at all, and in some can rotate in an irregular fashion corresponding to wave-functions intermediate between those for pure rotation and for pure oscillation; but that in hydrogen the molecules really can rotate quite freely, in all probability. In fact, the reasonable nature of the results obtained in Fowler's investigations are themselves fairly good evidence for the ability of the molecules of hydrogen to rotate in the crystal. But even if the molecules rotate, it certainly seems likely that under the influence of the fields of the neighbouring molecules a molecule in the crystal of hydrogen will possess a somewhat different moment of inertia from that which it has when in the gas. Such a difference may be quite small,† but if it exists at all, its effects on equilibria may well be large enough for experimental investigation.

We shall use the classical statistics, since the slight differences which would be introduced by the use of the correct Einstein-Bose statistics are no longer of interest to us, and the classical statistics are much simpler to handle. Using our old notation, with the difference that now $F(\theta)$ and $F'(\theta)$ refer to the molecules in the gas and $f(\theta)$ and $f'(\theta)$ to molecules in the crystal, the number of complexions in the assembly is

$$C = \left(\frac{1}{2\pi i}\right)^3 \iiint \frac{dx dx' dz \exp \{x F(z) G(z) + x' F'(z) G'(z)\}}{x^{X+1} x'^{X'+1} z^{E+1} \{1 - (x f(z) + x' f'(z)) \kappa(z)\}}.$$

* Pauling, 'Phys. Rev.' vol. 36, p. 430 (1930).

† Unfortunately, measurements of the Raman effect do not seem to have been performed upon crystalline hydrogen. But J. C. McLennan and J. H. McLeod ('Nature,' vol. 123, p. 160 (1929)) find in the case of liquid hydrogen Raman wave-numbers 354 cm.⁻¹ and 588 cm.⁻¹ corresponding to the transitions $j = 0 \rightarrow j = 2$, and $j = 1 \rightarrow j = 3$, respectively. These are to be compared with the wave-numbers 347 cm.⁻¹ and 578 cm.⁻¹ respectively obtained from band spectra, and indicate, possibly, a small diminution in the moment of inertia of a hydrogen molecule when it condenses from the gas into the liquid.

As before,

$$\bar{P} = \frac{\xi f(\theta) \kappa(\theta)}{1 - (\xi f(\theta) + \xi' f'(\theta)) \kappa(\theta)}; \quad \bar{P}' = \frac{\xi' f'(\theta) \kappa(\theta)}{1 - (\xi f(\theta) + \xi' f'(\theta)) \kappa(\theta)},$$

and also

$$\bar{N} = \xi F(\theta) G(\theta); \quad \bar{N}' = \xi' F'(\theta) G(\theta).$$

As before,

$$(\xi f(\theta) + \xi' f'(\theta)) \kappa(\theta) = 1.$$

Let $\bar{P}' = s\bar{P}$; then

$$\frac{\bar{N}'}{\bar{N}} = s \frac{F'(\theta) f(\theta)}{F(\theta) f'(\theta)}.$$

Let

$$F(\theta) = \sum_{j=0, 2, 4, \dots}^{\infty} (2j+1) e^{-j(j+1)\epsilon_g/kT}$$

$$f(\theta) = \sum_{j=0, 2, 4, \dots}^{\infty} (2j+1) e^{-j(j+1)\epsilon_c/kT}$$

with similar expressions for $F'(\theta)$ and $f'(\theta)$, summed this time over odd values of j . Then

$$\frac{\bar{N}'}{\bar{N}} = s e^{-2(\epsilon_g - \epsilon_c)/kT}$$

if $kT/6\epsilon_g$ and $kT/6\epsilon_c$ are small ($T < 100^\circ$ K. for hydrogen). We have

$$\bar{N} = \frac{1}{s+1} \frac{G(\theta)}{\kappa(\theta)}; \quad \bar{N}' = \frac{s}{s+1} \frac{G(\theta)}{\kappa(\theta)} e^{-2(\epsilon_g - \epsilon_c)/kT};$$

and if we suppose as before that $X' = 3X$ then it follows that

$$(14) \quad s = \frac{3}{1 - \frac{\bar{N}}{X} \{1 - \exp[-2(\epsilon_g - \epsilon_c)/kT]\}}$$

$$(15) \quad \frac{\bar{N}'}{\bar{N}} = \frac{3 \exp[-2(\epsilon_g - \epsilon_c)/kT]}{1 - \frac{\bar{N}}{X} \{1 - \exp[-2(\epsilon_g - \epsilon_c)/kT]\}}$$

and

$$(16) \quad \bar{N}' + \bar{N} = \frac{G(T)}{K(T)} \frac{1}{s+1} \{1 + s \exp[-2(\epsilon_g - \epsilon_c)/kT]\}.$$

Suppose first that $\epsilon_g > \epsilon_c$. Then we see from (14) that when the crystal is just starting to form, so that the ratio $\bar{N}/X$ is nearly unity, para-hydrogen will predominate over ortho-hydrogen in the crystal in a greater ratio than 3:1. If, on the other hand, $\epsilon_g < \epsilon_c$, then when the crystal is just starting

for form the ratio will be smaller than 3 : 1. We could thus investigate experimentally whether or not a difference existed between the moments of inertia in the gas and in the crystal, by starting with ordinary hydrogen and cooling it by passing it into a tube cooled with solid hydrogen ; stopping the process before much of the ordinary hydrogen had solidified. A determination of the ratios of the two sorts of hydrogen in the crystals would then, when we used equation (14), furnish us with information about the moments of inertia. This experiment would be an interesting one to perform. As the hydrogen continues to solidify, of course the ratio in the crystal approaches 3 : 1. The lower the temperature, the greater should the ratio deviate, as the crystal just starts to form, from 3 : 1, if $\epsilon_g \neq \epsilon_c$.

If we are interested in the proportions of the two sorts of hydrogen in the gas, we can use equation (15). Equation (16) enables us to investigate the effect of changes in the moment of inertia upon the chemical constant of hydrogen vapour.

§ 6. *The Entropy of the Different Sorts of Hydrogen Crystals at the Absolute Zero of Temperature.*

In modern statistical mechanics the entropy of a system appears* as the quantity $S = k \log C$, where C is the total number of permissible linearly independent wave-functions which can represent the assembly. By "permissible" we mean simply that they are to have the proper symmetry properties. Thus for an assembly of hydrogen molecules each wave-function, as we have mentioned in a previous section, must be symmetric in all of the molecules. As a function of the state of the assembly, satisfying the equation $dQ = T dS$, where dQ is the thermal energy added to the assembly, the solution S is of course not unique ; but the convention has been made of taking the additive constant to be zero.

Consider a gram molecule of para-hydrogen in the crystalline form at the absolute zero. We may neglect the normal modes of vibration of the crystal, as far as the number of wave-functions is concerned at the absolute zero. Each molecule of the crystal, being in the zero'th rotational state, is capable of representation by just a single wave-function. Thus there is only one wave-function for the entire crystal in this state of minimum energy. The entropy of crystalline para-hydrogen at the absolute zero per gram molecule is accordingly.

$$(17) \quad S_p = k \log 1 = 0.$$

* Fowler, "Statistical Mechanics," pp. 533, 534.

Consider next a crystal composed of a gram molecule of ortho-hydrogen at the absolute zero. Each molecule is now in the first rotational state and is capable of being represented by any one of nine wave-functions, corresponding to three possible eigenvalues of the z component of nuclear rotational angular momentum and to three possible eigenvalues of the z component of resultant nuclear spin angular momentum. The number of permissible linearly independent wave-functions is now simply 9^N where N is Avogadro's number. Hence for this crystal

$$(18) \quad S_0 = kN \log 9 = R \log 9.$$

Finally, consider a crystal of ordinary hydrogen at the absolute zero, composed of $N/4$ molecules of para-hydrogen and $3N/4$ molecules of ortho-hydrogen. The number of wave-functions is now

$$C = 9^{3N/4} 1^{N/4} \frac{N!}{(3N/4)! (N/4)!}$$

and by the use of Stirling's asymptotic formula for factorials we find, neglecting absolutely trivial terms, that

$$(19) \quad \begin{aligned} S_0 &= k \log C \\ &= \frac{3}{4} R \log 3 + R \log 4. \end{aligned}$$

The values (17) and (19) are in complete agreement with the results of D. MacGillavry,* who finds, using a thermodynamic argument, that the difference between the entropies of a gram molecule of ordinary hydrogen and a gram molecule of para-hydrogen at the absolute zero is the value given in equation (19). The method used in this paper, however, is a simpler method than MacGillavry's of establishing this result.†

The writer wishes to thank Mr. R. H. Fowler for his criticisms and for his encouragement.

* D. MacGillavry, 'Phys. Rev.', vol. 36, p. 1398 (1930).

† MacGillavry shows by thermodynamic arguments that this difference between the entropies at the absolute zero of para-hydrogen and ordinary hydrogen is equivalent to the assumption that at high temperatures, when transitions between para- and ortho-states can occur freely, the state and in particular the entropy of hydrogen gas is the same as it would be, at the same temperature, if such transitions could not occur.

The Scattering of Slow Alpha Particles by Helium.

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[PLATE 6.]

1. Gordon* has proved that the scattering of particles by an inverse square field is the same on the wave mechanics as on the classical theory. Mott† has however shown, from consideration of the symmetry of the wave functions, that the scattering is quite different from the classical when the scattering and scattered particles are identical. The scattering of alpha particles by helium is typical of the case of the collision of identical particles that have no spin and obey the Einstein-Bose statistics. For this case, the expression given by Mott for the number of alpha particles scattered between angles θ , and $\theta + d\theta$, in going a distance dr in a gas containing n atoms per unit volume, is

$$N d\theta dr = \frac{4\pi n N_0 e^4}{m^2 v^4} \{ \text{cosec}^4 \theta + \sec^4 \theta + 2 \text{cosec}^2 \theta \sec^2 \theta \cos u \} d\theta dr, \quad (1)$$

where

$$u = \frac{8}{137} \frac{c}{v} \log \cot \theta, \quad (2)$$

and N_0 is the total number of incident particles, v , m and e , their initial velocity, mass and charge and c the velocity of light.

On classical mechanics the number of alpha particles scattered through the angle θ is given by the first term in the bracket, while the number of helium atoms projected at this angle is given by the second term. The last term, which arises from the interference in co-ordinate space of the waves representing these two streams of particles, is an oscillating function of θ and v , and so gives rise to an interference pattern which varies in scale with the velocity. The intensity of the scattering at $\theta = 45^\circ$ is double the classical for all values of the velocity. The oscillations of intensity with varying θ are more marked and closer together, the lower the velocity. In fig. 1, curves (a), (b) and (c), is shown the variation of scattered intensity with θ for velocities of 10^8 , 2×10^8 and 8×10^8 cm. per second, corresponding to ranges in air at

* Gordon, 'Z. Physik,' vol. 48, p. 180 (1928).

† Mott, 'Proc. Roy. Soc.,' vol. 126, p. 259 (1930).

N.T.P. of 0.4, 1.0 and 7.7 mm. The dotted line shows the classical intensity. In the first case there are three minima, in the next, one, and in the last, none.

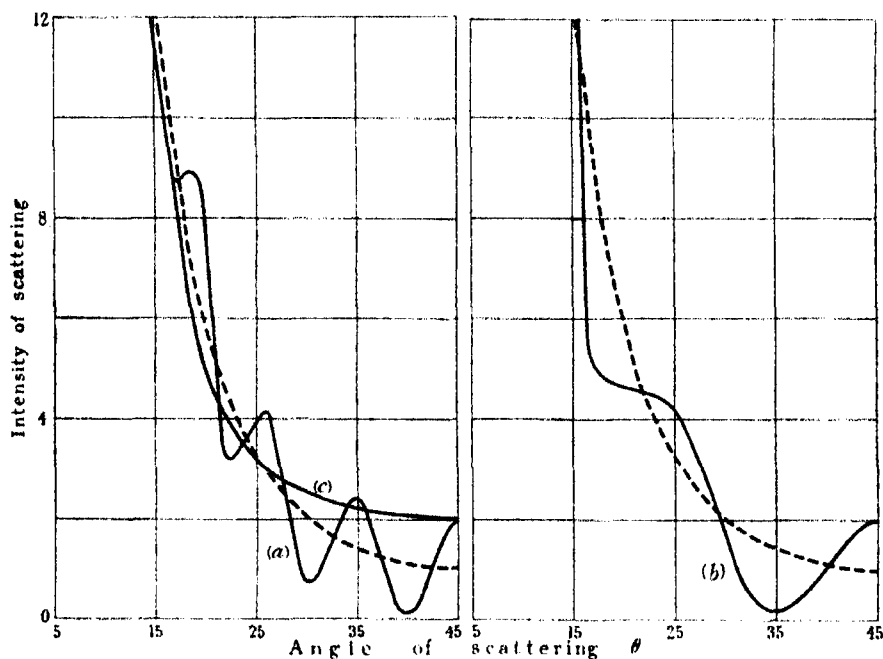


FIG. 1.

The relative amplitude of the oscillations decreases rapidly as θ is reduced. It is interesting to note that for small velocities the angular width of these fringes is given approximately by $\Theta = \lambda/d$, where λ is the De Broglie wave-length of the alpha particle with its initial velocity, and d is half the closest distance of approach. The angular width of the fringes is therefore just that of the pattern due to the diffraction of a wave of wave-length λ by an aperture or screen of dimensions d . As the velocity is reduced λ increases as $1/v$ but d increases as $1/v^2$ leading to the contraction in the width of the fringes.

Mott's theory has been tested by Chadwick* using the scintillation method. The number of alpha particles scattered by helium atoms at an average angle of 45° were determined as a function of their velocity. The earlier work of Rutherford† and Chadwick had shown that the scattering of fast particles at 45° was greatly in excess of the classical value. This was attributed to the structure of the particles; that is the assumption was made that the forces

* Chadwick, 'Proc. Roy. Soc.,' A, vol. 128, p. 114 (1930).

† Rutherford and Chadwick, 'Phil. Mag.,' vol. 4, p. 605 (1927).

between them when at the small distances reached in a fast collision, were no longer those of the inverse square. This law of force must, however, be valid at sufficiently large distances. Thus, as the velocity of the particles is reduced, the ratio of the observed scattering to that calculated classically for the law of the inverse square should tend to unity, while according to Mott's theory it should tend to 2. Chadwick in fact found that this ratio did approach the value 2 at the lowest velocity (8.5×10^8 cm. per second) used. Slower particles could not be utilised owing to the difficulty of counting the scintillations.

The calculation of the absolute magnitude of the scattered intensity was made by comparison with the scattering by argon, which was assumed, on the basis of some earlier measurements of Rutherford and Chadwick, to scatter classically. By using a Wilson chamber the scattering can, however, be followed down to a velocity of 10^8 cm. per second, corresponding to a range of $\frac{1}{2}$ mm. in air at N.T.P., that is to velocities eight smaller than is possible with the scintillation method. At such low velocities the maxima and minima predicted by Mott's theory are very marked, so that a very definite test of the theory is possible. The further advantage that the absolute values of the scattered intensity can be directly determined is offset by the large chance variation of the intensity due to the small number of measured collisions. For these slow particles the closest distance of approach is so large that there is no possibility of any deviation from the inverse square law complicating the scattering. The actual apsidal distance for a particle of $\frac{1}{2}$ mm. range which makes a 40° collision is about 5×10^{-11} cm.

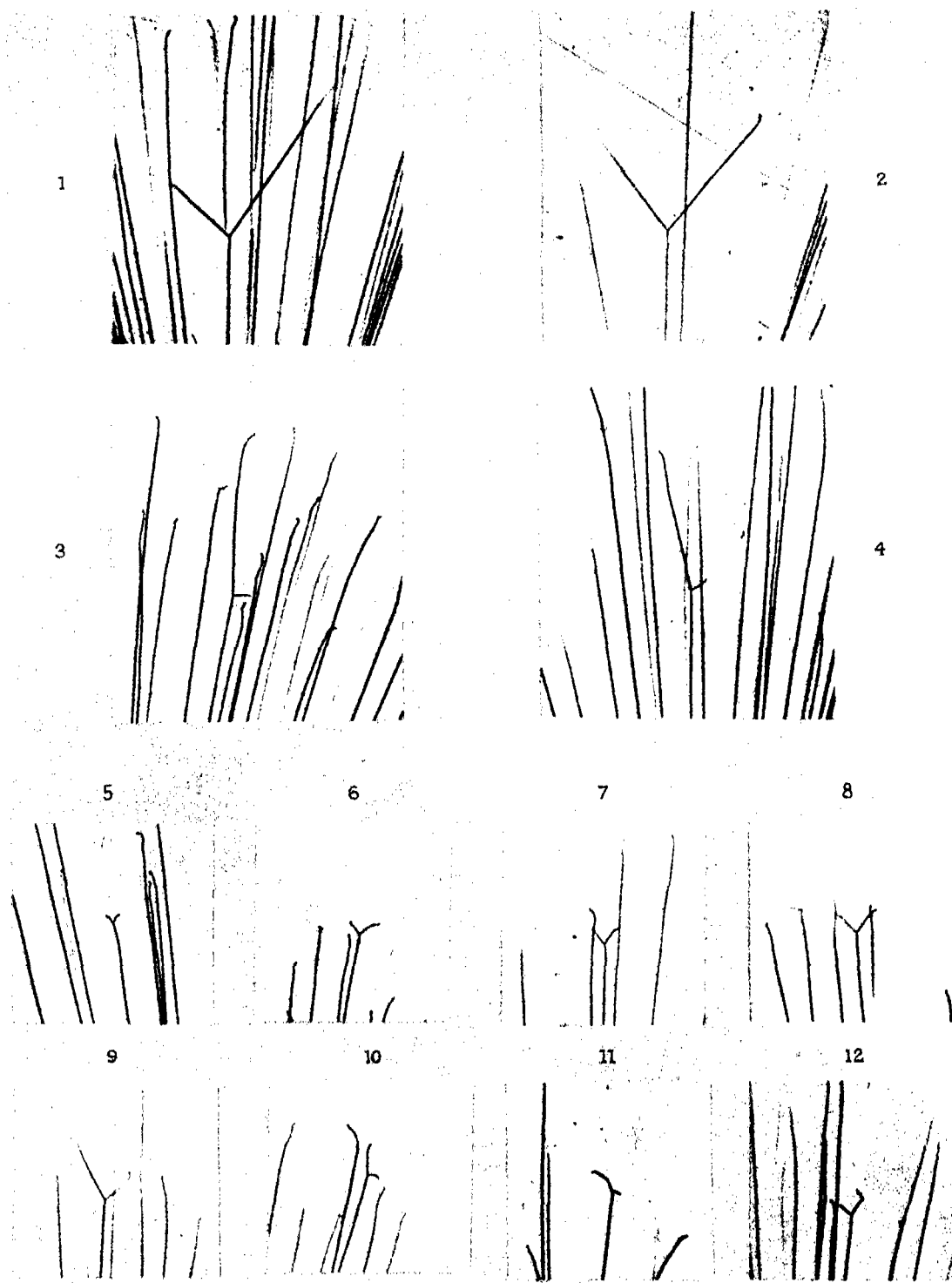
2. *The Experimental Method.*

Photographs of about 50,000 alpha rays from polonium were made using an automatic Wilson chamber,* containing a mixture of helium and oxygen, and measurements were made of the forks due to the collision of alpha particles with helium atoms. From these measurements were calculated the lengths R_θ and R_ϕ of the two arms of the fork and the angles θ and ϕ between them and the stem of the track. For an elastic collision between two identical particles $\theta + \phi = \pi/2$, and

$$v_\theta/v_\phi = \tan \theta, \quad (3)$$

where v_θ and v_ϕ are the velocities of the two particles after the collision. The test of the first relation, together with that for the coplanarity of the fork, serves to identify a collision as an elastic one with a helium atom. But when

* Blackett, 'Proc. Roy. Soc.,' A, vol. 123, p. 613 (1929).



Collisions of Alpha Particles with Helium Atoms.

The photographs show the tracks 3·7 as large as they would be in air at N.T.P.

(Facing p. 383.)

one arm is very short, its direction cannot be determined with sufficient accuracy to make this test feasible. In this case use was made of the known relation between the range and velocity of the particles (see below) to calculate v_θ/v_ϕ from the ranges, and to compare it with the ratio as calculated from the observed value of θ . This method allows collisions with helium atoms to be distinguished from those with oxygen atoms, even when ϕ is not measurable. In every case the initial velocity of the particle is deduced from the relation $v^2 = v_\theta^2 + v_\phi^2$ and the corresponding "initial" range R determined.

Since the two particles colliding are identical, it is in principle impossible to determine whether the collision corresponds to a deflection of θ or ϕ . If the convention is adopted of calling the smaller of the two angles θ , then no values of θ greater than 45° occur. The result of the measurements is the pair of values of θ and R for each of the measured helium collisions. The values of the latter are all reduced to the equivalent ranges in air at 15° C. and 760 mm. Since collisions of sufficiently small angle are not observable, it is necessary to have a criterion to govern the decision to measure a fork. The one adopted is that all forks are counted if the length of the shorter arm is equal or greater than some definite value; actually the criterion used was $R_\phi > 0.20$ mm. in air at N.T.P. Further no tracks were counted for which the initial range R , was less than 0.5 mm. or greater than 8.0 mm.

To calculate the expected number of scattered particles, it is necessary to know accurately how the velocity of a particle varies along the last few millimetres of its track. This can be determined up to about 4 mm. from the end by using Briggs' results for air,* corrected for the change of relative stopping power of the helium-oxygen mixture relative with air. The data for this are available from the measurements of Gurney† and Bates.‡ To extend the curve up to the extreme end of the track, use is made of a method described in a former paper.§ Measurements of θ , R_θ and R_ϕ are made for a fork for which $R_\theta > 4$ mm. and $R_\phi < 4$ mm. (photographs Nos. 3 and 4). From the value of R_θ , the velocity v_θ is obtained using the known relation between the two quantities, and then v_ϕ is calculated from (3), thus giving, with the observed value of R_ϕ , a new point on the range velocity curve. By this means an accurate determination of the range velocity relation right up to the end of the range has been made. From these new results, which will shortly be described in detail,

* Briggs, 'Proc. Roy. Soc.,' A, vol. 114, p. 341 (1927).

† Gurney, 'Proc. Roy. Soc.,' A, vol. 107, p. 340 (1925).

‡ Bates, 'Proc. Roy. Soc.,' A, vol. 106, p. 622 (1924).

§ Blackett, 'Proc. Roy. Soc.,' A, vol. 103, p. 62 (1923).

the following table gives the results relevant to the present discussion. The probable error of these velocity determinations is a few per cent.

Table I.

Range in air at 760 mm., 15° C. in millimetres	0.5	1.0	2.0	3.0	4.0	6.0	8.0	10.0
Velocity in centimetres per second $\times 10^{-8}$	1.20	2.00	3.30	4.35	5.35	6.90	8.20	9.25

3. The Results.

For each of the 428 measured forks found among the 56,820 photographed tracks, a dot, corresponding to the observed values of θ and R , was placed on a diagram with these quantities as co-ordinates (fig. 2). The density of dots is then a measure of the scattered intensity.*

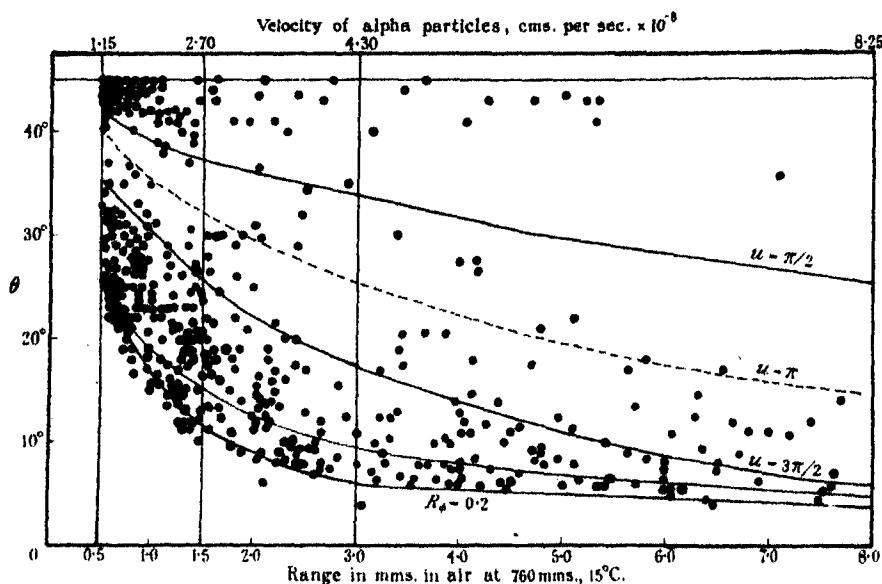


FIG. 2.

* Note.—The diagram should contain a dot for all those and only those forks which satisfy the conditions, $0.5 < R < 8$ mm., $R_\phi > 0.2$ mm. It will, however, be noticed that some dots fall below the line $R_\phi = 0.2$ mm. This is due to the fact that though the criterion that $R_\phi > 0.2$ mm. was used to decide whether a fork should be counted, the actual dot was plotted at the measured value of θ and R . If the measurement of the three quantities θ , R and R_ϕ were exact, a fork for which $R_\phi > 0.2$, would, when plotted as the point (θ, R) , lie above the line $R_\phi = 0.2$ mm. But as the measurements are not exact some of such points will lie below the line. It is legitimate to count these points as belonging to the nearest cells above the line, and these dots have in fact been included in

It is immediately evident that the observed distribution is incompatible with classical scattering, which predicts a steady decrease in the number of collisions with increasing θ . On the other hand the distribution is seen at once to be in complete qualitative agreement with Mott's theory, which predicts a maximum of double the classical for $\theta = 45^\circ$, and a minimum along the line (shown dotted), defined by $u = \pi$, that is, $\cos u = -1$. As R increases from $\frac{1}{2}$ mm. the deep minimum of nearly zero intensity at about $\theta = 40^\circ$, moves to smaller values of θ , and becomes shallower. The obvious general agreement of the experimental results with the theory is very striking. The second minimum cannot be observed as it exists only for ranges less than 1 mm. and also lies very close to the limit of observation given by the line $R_\phi = 0.2$ mm. The apparent slight minimum about the point $R = 1.2$, $\theta = 20^\circ$ is probably to be attributed to chance variations.

A quantitative comparison with the theory is obtained by dividing the diagram into cells and comparing the observed and calculated numbers of dots in each cell.

The boundaries of the cells were chosen in the following way. The range of R from 0.5 to 8.0 mm. was divided more or less arbitrarily by the ordinates at 1.5 and 3.0 mm., to give suitably sized cells, containing a convenient number of dots. The limits were thus 0.5, 1.5, 3.0 and 8.0 mm. The limiting values of θ were determined by putting $\cos u = 0$, that is, the horizontal divisions between the cells were chosen as the lines along which the quantum theory scattering is equal to the classical. These lines are shown full on the diagram. Between $\theta = 45^\circ$ and the line given by $u = \pi/2$, the theoretical intensity is everywhere greater than the classical, since here $\cos u$ is positive; between the latter line and that given by $u = 3\pi/2$, it is everywhere less, since here $\cos u$ is negative; between the last and the line defined by $R_\phi = 0.2$ mm. which marks the adopted lower limit of the diagram, it is partly greater, and partly smaller, but the calculated intensity variations are too small to be detected with so few observations.

The expected number in any cell is

$$N_c = \iint N(\theta, r) d\theta dr,$$

with the integration limits given by the cell boundary.

the numbers given in Table II. It would be certainly theoretically preferable to use instead the criterion that the point corresponding to the measured values of θ and R should lie above the curve $R_\phi = 0.2$ mm. Though the former criterion was adopted owing to its greater convenience, the experience of this work has emphasised the advantage of the latter (see conclusion of section 3).

This gives

$$N_q = K_1 K_2 w \quad (4)$$

where

$$K_1 = 4\pi N_0 n_0 e^4 10^{22}/m^2, \quad (5)$$

$$K_2 = f p T_0 L / T R_0 \quad (6)$$

and

$$w = \int_{R_1}^{R_2} \frac{dR}{V^4} \int_{\theta_1}^{\theta_2} [\operatorname{cosec}^4 \theta + \sec^4 \theta + 2 \operatorname{cosec}^2 \theta \sec^2 \theta \cos u] d\theta, \quad (7)$$

where as before

$$u = \frac{8}{137} \frac{c}{v} \log \cot \theta.$$

In these equations n_0 is the number of molecules in 1 c.c. at 760 mm. 15°C. , R is the range in air under the same conditions, $V = v \times 10^8$, and f = fraction of helium in gas mixture, p = final pressure in chamber in atmospheres, L = length of tracks in chamber, R_0 = range of alpha particles from polonium in air at 760 mm. 15°C.

Using the accepted values of e and m for the alpha particle, and of n_0 , and the following quantities determined experimentally, N_0 = number of tracks = 56,820, $f = 0.65$, $L = 10.0 \text{ cm.}$, $R_0 = 3.87 \text{ cm.}$, $p = 0.80$, $T = 15^\circ \text{C.}$, we get

$$K_1 = 3500$$

$$K_2 = 1.34,$$

so that

$$N_q = 4700 w.$$

Note.—The number of helium molecules in 1 c.c. of the gas in the chamber is $n = f p T_0 n_0 / T$, and the equivalent range dR in air at N.T.P. is $dR = R_0 dr / L$, so that $n dr = K_2 n_0 dR$.

The integrations to give w have to be carried out graphically, using in the integration with respect to R the experimental relation between v and R given in Table I. The limits θ_1 and θ_2 , both of which, in general, depend on R , are taken from the cell boundaries in the diagram. The numbers N_q expected on the classical theory were calculated by putting $\cos u = 0$ in (7). In this case the first integral is obtained directly. The final results are shown in fig. 3, which is a diagrammatic representation of the cells. The observed numbers are shown in *block* figures, the calculated numbers on the quantum theory in small figures, and the calculated classical numbers in brackets.

Neglecting for the moment the lower three cells, excellent agreement is found between the observed numbers and those calculated on the quantum theory. The actual observed numbers will, of course, be liable to chance

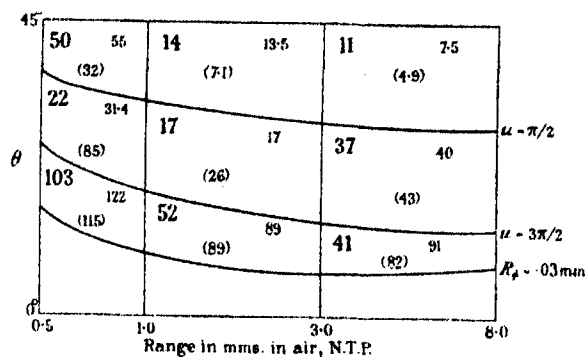


Fig. 3.

variations. If N_r is the observed number of dots in the r th cell of a set of n cells and if $\bar{N}_r$ is the mean number, over a large number of experiments, then the mean value of the quantity

$$F = \frac{1}{n-1} \sum \frac{(N_r - \bar{N}_r)^2}{\bar{N}_r},$$

taken over a large number of experiments, is unity.

If in this expression $\bar{N}_r$ is given the calculated theoretical value for each cell, a value of F in the neighbourhood of unity will indicate a distribution quite consistent with the calculated average. For the upper six cells, F has the value 1.04 when the average values predicted by the quantum theory are used and a value 15.3 for the classical figures. The observed distribution is therefore a probable one if the quantum theory of the scattering is correct, but a most improbable one if the classical theory is right.

If the lower boundary of the lowest row of cells is taken as the line $R_p = 0.2$ mm., the numbers expected on the quantum and classical theories are nearly the same, but over double the observed numbers. The numbers for the three lower cells are:—

Table II.

N observed	151	79	73
N_q	361	160	162
N_c	347	160	162

It is very improbable that this is to be taken as indicating a real reduction in scattering below that calculated, as the effect of the electronic screening only enters at much smaller angles. It is probably to be attributed to the unexpected and disappointing failure to count more than a fraction of the forks

lying just above the criterion line. It is possible that a large number of such small angle collisions with helium atoms were wrongly attributed to collisions with oxygen atom and so were not counted. It must be remembered that the limiting spur length of 0.2 mm. is only about double the breadth of the tracks so that exact length measurements are difficult, and that it is through the length measurements that the possibility of distinguishing between small angle helium and oxygen collisions depends. The procedure adopted was to raise arbitrarily the lower limit of the lower right-hand two cells from the line $R_\phi = 0.2$ to the line $R_\phi = 0.3$ and the lower limit of the left-hand lower cell to the line joining the points $R = 0.5$, $\theta = 25^\circ$ to $R = 1.5$, $\theta = 15^\circ$. The calculated and observed numbers for the reduced cells so formed are given on the diagram. The agreement with the left-hand cell is good, but the discrepancy for the others still marked, so that it must be assumed that many collisions above this new line were still being missed.

Taking the nine cells as a whole the agreement obtained with Mott's theory is very satisfactory. Since the scattered intensity is approximately proportional to $1/v^4$, the numerical agreement obtained gives strong confirmation of the accuracy of the velocity determination results given in Table I.

Summary.

A Wilson chamber was used to investigate the scattering of slow alpha particles in helium. The results are in excellent agreement with Mott's theory.

We are indebted to the Department of Scientific and Industrial Research for a grant to one of us (F. C. C.) and for a grant to meet some of the cost of the apparatus.

Description of Photographs.

No.	1	2	3	4	5	6	7	8	9	10	11	12
ϕ°	35	40	11	13	44	42	40	42	32	20	21	30
R, mm	14	13	7.2	5.7	0.7	1.2	1.4	2.0	4.0	1.7	1.4	1.5

The ranges are in millimetres of air at N.T.P.

Only one of the two photographs of each track is reproduced. All the photographs reproduced are of tracks whose planes are roughly at right angles to the axis of the camera, so that the apparent angles do not differ very much from the real angles.

It will be noticed that the ends of many of the tracks (*e.g.*, Nos. 10 and 11) are sharply curved, so that an exact determination of the angles becomes difficult. The origin of this curvature is under investigation.

On the Force Required to Stop a Moving Electrified Sphere.—II.

By G. F. C. SEARLE, Sc.D., F.R.S., University Lecturer in Experimental Physics, Cambridge.

(Received June 18, 1930.)

§ 1. *Introduction.*—Let an electrified sphere be in uniform rectilinear motion with velocity u , less than v the velocity of light, up to the time $t = 0$. At $t = 0$ let the sphere be suddenly stopped and then be held at rest.* In consequence of the stopping, each element dQ of charge gives rise to a spherical electro-magnetic wave centered at dQ and of radius vt at time t . This wave acts on all the elements of the charge which it meets at time t ; since the electric force in the wave has a forward component in the direction of u , the sphere experiences a resultant force urging it forward. This force must be resisted by an equal force F applied in the opposite direction, if the sphere is to remain at rest. No waves cut the sphere after a time $2a/v$, where a is the radius of the sphere, and hence the force vanishes when $t > 2a/v$.

The value of F for the special case when $u = v$ was given in these 'Proceedings'† in 1907 for a sphere with a surface charge and for a sphere with a volume charge. The value of F for the general case when $u < v$ is obtained in the present paper for a sphere with a surface charge.

§ 2. *Wave due to Stopping a Point-charge.*—If a point-charge q which moves along Ox , the axis of x , have its velocity suddenly changed from u to zero at O at time $t = 0$, the electro-magnetic field outside the spherical wave of radius vt centred at O is the same as if q had continued to move with velocity u . The electric force in this field is radial to the point A on Ox which q would have reached at time t , if it had not been stopped; thus $OA = ut$. Though the electric force E is radial to A , its value depends upon the angle β between the radius from A and Ax . We have‡

$$E = \frac{qv(v^2 - u^2)}{KR^2(v^2 - u^2 \sin^2 \beta)^{3/2}}, \quad (1)$$

* It may be stated, in response to a suggestion by a referee, that the exact conditions assumed in the problem are not capable of realisation. The sphere on which the charge is spread is ideal; it has no mass, it is rigid and it does not affect the electric field. The agent supplying the stopping force is such that it does not affect the electrical conditions.—September 29, 1930.

† 'Proc. Roy. Soc.,' A, vol. 79, p. 550 (1907).

‡ Heaviside, "The Electrician," December 7, 1888, or "Electrical Papers," vol. 2, p. 511.

where R is the distance from q , and K is the dielectric constant. The magnetic force is in circles about Ox as axis. Inside the wave the field is the same as if q had always been at rest at O . This field is the ordinary electrostatic field and the electric force is radial to O .

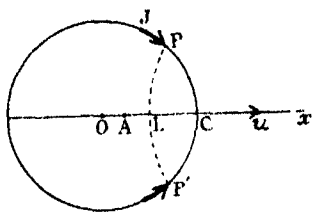


FIG. 1.

The flux of electric displacement outwards from the convex surface of the spherical cap formed by the revolution of the arc PCP' (fig. 1) about Ox is*

$$\frac{q(u+v)(1-\cos\gamma)}{2(v-u\cos\gamma)},$$

where $POC = COP' = \gamma$. The flux into the concave surface of the cap from q at O is $\frac{1}{2}q(1-\cos\gamma)$. Hence the outward flux from the convex surface exceeds that into the concave surface by $qu\sin^2\gamma/2(v-u\cos\gamma)$.

Since there is no charge on the cap, the difference must be balanced by a flux into PLP' , the edge of the cap. This flux of electric displacement is in the wave and along great circles whose planes contain Ox and is accompanied by magnetic force in small circles having C for pole. If the flux of displacement per unit length of the edge of the cap be J , the flux into the cap by its edge is $J \cdot 2\pi r \sin\gamma$, where $r = vt$. Equating this to the excess of the outward over the inward flux, we find†

$$J = qu \sin\gamma / 4\pi r (v - u \cos\gamma). \quad (2)$$

If, instead of a point-charge, we have an elementary charge dQ , of thickness p measured parallel to OP , the tangential flux of displacement in the wave near P will be spread over a thickness p . If the electric force in the wave at P be dE , we have $KdE/4\pi = J/p$. If dE_x be the component of dE in the direction Ox , $dE_x = dE \sin\gamma$, and hence

$$dE_x = \frac{u \sin^2\gamma}{Kr(v-u\cos\gamma)} \cdot \frac{dQ}{p}. \quad (3)$$

This component is in the forward direction for all values of γ .

§ 3. *Force required to stop a sphere of radius a with a Surface-charge Q .—*

* Searle, 'Phil. Mag.', vol. 13, p. 121 (1907).

† Searle, 'Phil. Mag.', vol. 13, p. 121 (1907). This expression was first given by Heaviside, 'The Electrician,' October 11, 1901. See also "Electro-magnetic Theory," vol. 3, p. 127.

Let O (fig. 2) be the centre of the charged sphere after it has been brought to rest, Ox the direction of the original velocity u . Let P be a point on the surface of the sphere and let $POx = \theta$. About P as centre describe two spheres of radii r and $r + dr$ cutting the sphere in circles through S and S'. Let $SPO = \phi$, $S'PO = \phi + d\phi$. Let N be a point on the band defined by these circles and let the plane NPO make angle ψ with the plane POx. Since $r = 2a \cos \phi$, $dr = -2a \sin \phi d\phi$. The angle which S'S subtends at O is double the angle it subtends at P and hence $SS' = -2ad\phi$. If the charge on that element of the band which is defined by the planes ψ and $\psi + d\psi$ be dQ ,

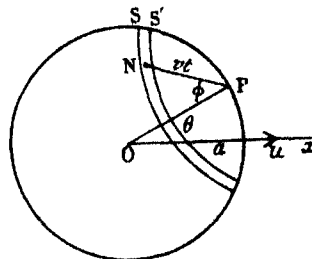


FIG. 2.

$$dQ = \sigma (-2ad\phi) r \sin \phi d\psi.$$

For the thickness, p , of the element measured parallel to NP or r we have

$$p = dr = -2a \sin \phi d\phi.$$

The surface density σ is given by $\sigma = Q/4\pi a^2$, and thus

$$\frac{dQ}{p} = \frac{Qr d\psi}{4\pi a^2}. \quad (4)$$

If dE_x be the component parallel to Ox of the electric force at P due to the wave arising from dQ at N, we have, by (3) and (4),

$$dE_x = \frac{Qu \sin^2 \gamma \cdot d\psi}{4\pi Ka^2 (v - u \cos \gamma)}. \quad (5)$$

Of the whole surface of the sphere it is only the band defined by r , where $r = vt$, which acts upon P by waves at time t , and hence we obtain the whole value of E_x at P due to waves by integrating (5) with respect to ψ from 0 to 2π .

Now $r \cos \gamma$ is the projection of NP (not PN) upon Ox and thus

$$\cos \gamma = \cos \theta \cos \phi + \sin \theta \sin \phi \cos \psi. \quad (6)$$

When $u = v$, $u \sin^2 \gamma / (v - u \cos \gamma) = 1 + \cos \gamma$. In this case

$$\begin{aligned} E_x &= \frac{Q}{4\pi Ka^2} \int_0^{2\pi} (1 + \cos \theta \cos \phi + \sin \theta \sin \phi \cos \psi) d\psi \\ &= \frac{Q}{2Ka^2} (1 + \cos \theta \cos \phi). \end{aligned}$$

The resultant force on the sphere due to waves is F , where, in this special case,

$$F = \int_0^\pi \frac{E_x Q}{4\pi a^2} 2\pi a^2 \sin \theta d\theta = \frac{Q^2}{4Ka^2} \int_0^\pi (1 + \cos \theta \cos \phi) \sin \theta d\theta = \frac{Q^2}{2Ka^2}. \quad (7)$$

The force is therefore constant for the whole time $2a/v$ of its duration. This result was found in 1907* by the same method.

We now return to the general case when $u < v$. We find by (5) and (6)

$$E_x = \frac{Q}{4\pi Ka^2 \sin \theta \sin \phi} \cdot I, \quad (8)$$

where

$$I = \int_0^{2\pi} \frac{A - B \cos \psi - C \cos^2 \psi}{D - \cos \psi} d\psi, \quad (9)$$

and

$$A = 1 - \cos^2 \theta \cos^2 \phi, \quad B = 2 \cos \theta \cos \phi \sin \theta \sin \phi, \quad C = \sin^2 \theta \sin^2 \phi,$$

$$D = (v - u \cos \theta \cos \phi)/(u \sin \theta \sin \phi).$$

We easily find

$$D^2 - 1 = \{h^2 + (v^2 - u^2) \sin^2 \phi\}/(u^2 \sin^2 \theta \sin^2 \phi), \quad (10)$$

where

$$h = v \cos \phi - u \cos \theta, \quad (11)$$

and thus $D^2 > 1$. Hence

$$\int_0^{2\pi} \frac{d\psi}{D - \cos \psi} = \frac{2\pi}{(D^2 - 1)^{1/2}}. \quad (12)$$

Further,

$$A - BD - CD^2 = -(v^2 - u^2)/u^2. \quad (13)$$

Now

$$\begin{aligned} A - B \cos \psi - C \cos^2 \psi &= (A - BD - CD^2) \\ &\quad + (B + 2CD)(D - \cos \psi) - C(D - \cos \psi)^2, \end{aligned}$$

and thus we have

$$I = I_1 - I_2, \quad (14)$$

where

$$I_1 = \int_0^{2\pi} \{B + 2CD - C(D - \cos \psi)\} d\psi,$$

$$I_2 = -(A - BD - CD^2) \int_0^{2\pi} \frac{d\psi}{D - \cos \psi}.$$

Using the values of B, C, D , we have

$$I_1 = 2\pi(B + CD) = 2\pi \sin \theta \sin \phi (\cos \theta \cos \phi + v/u). \quad (15)$$

* Searle, 'Proc. Roy. Soc.,' A, vol. 79, p. 560 (1907).

By (10), (11), (12) and (13),

$$I_2 = \frac{2\pi (v^2 - u^2) \sin \theta \sin \phi}{u \{h^2 + (v^2 - u^2) \sin^2 \phi\}^{1/2}}. \quad (16)$$

Hence, by (8), (15) and (16),

$$E_x = \frac{Q}{2Ka^2} \left[\cos \theta \cos \phi + \frac{v}{u} - \frac{v^2 - u^2}{u \{h^2 + (v^2 - u^2) \sin^2 \phi\}^{1/2}} \right]. \quad (17)$$

If F be the resultant force on the sphere due to the waves,

$$F = \int_0^\pi \frac{E_x Q}{4\pi a^2} 2\pi a^2 \sin \theta d\theta = \frac{Q^2}{4Ka^2} \left\{ M - \frac{v^2 - u^2}{u^2} N \right\},$$

where

$$M = \int_0^\pi (\cos \theta \cos \phi + v/u) \sin \theta d\theta = 2v/u,$$

$$N = \int_0^\pi \frac{u \sin \theta d\theta}{\{h^2 + (v^2 - u^2) \sin^2 \phi\}^{1/2}}.$$

By (11), $u \sin \theta d\theta = dh$. When $\theta = 0$, $h = v \cos \phi - u$, and, when $\theta = \pi$, $h = v \cos \phi + u$. Thus

$$\begin{aligned} N &= \left[\log \{h + \sqrt{h^2 + (v^2 - u^2) \sin^2 \phi}\} \right]_{v \cos \phi - u}^{v \cos \phi + u} \\ &= \log \frac{v + u}{v - u}. \end{aligned}$$

Hence

$$F = \frac{Q^2}{2Ka^2} \left\{ \frac{v}{u} - \frac{v^2 - u^2}{2u^2} \log \frac{v + u}{v - u} \right\}. \quad (18)$$

This force is constant for the whole time $2a/v$ of its duration. The force does not exist when $t > 2a/v$, because then no waves cut the sphere.

The x -component of the electric force at P due to *waves* is given by (18). The element of charge at P is also acted on by the charges on the sphere whose distances from P are less than vt , as well as by those whose distances are greater than vt . The elements within the distance vt act on the element at P according to the ordinary electrostatic law, and the element at P acts on them in the same manner. The elements outside the distance vt act on the element at P in the same way as if they had continued to move with the velocity u . By (1), the electric force due to a moving charge is unchanged if we put $\pi + \beta$ for β , and hence the actions between the element at P and the elements outside the distance vt are in equilibrium. Thus the actions between the element at P and those elements whose distances from P are less than vt and also the actions

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between the element at P and those elements whose distances from P are greater than vt may be left out of account when we estimate the force experienced by the whole sphere.

At the point P there is at time t magnetic induction due to the waves and also due to those elements whose distances from P are greater than vt . But the charge at P is at *rest* and hence the magnetic induction gives rise to no mechanical force.

The force required to stop the sphere is therefore given by (7) for the special case when $u = v$, and by (18) for the general case when $u < v$.

§ 4. *Paul Hertz's Method.*—The value of F given by (18) was found* in 1907 by a different method depending upon a knowledge of the energy W' and the momentum† P' carried off to infinity in the compound wave formed when the sphere is stopped at $t = 0$ for a time t and is then re-started with velocity u in the original direction. It was shown that

$$F = \frac{d}{dt} \left(\frac{W'}{u} - P' \right). \quad (19)$$

The method employed was an extension of that by which Dr. Paul Hertz‡ found the driving force F_1 required at time t when a charged sphere is set into motion with uniform velocity u at time $t = 0$. He showed that

$$F_1 = \frac{1}{u} \frac{dW_1}{dt}, \quad (20)$$

where W_1 is the energy carried off to infinity by the compound wave formed when the sphere is started with velocity u at $t = 0$ and at time t is suddenly stopped. From $t = 0$ to $t = 2a/(v + u)$, F_1 has the value given by (18). From $t = 2a/(v + u)$ to $t = 2a/(v - u)$, F_1 is a complicated function of t . When $t > 2a/(v - u)$, $F_1 = 0$.

* Searle, 'Proc. Roy. Soc.,' A, vol. 79, p. 555 (1907).

† The momentum per unit volume is $(\mu K/4\pi) \mathbf{VEH}$, where $\mathbf{VEH}$ is the vector product of the electric and magnetic forces.

‡ See Searle, 'Proc. Roy. Soc.,' A, vol. 79, p. 551 (1907).

Interferometric Measurements in the Arc Spectrum of Iron.

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Introduction.

At the 1928 Meeting of the International Astronomical Union at Leiden, it was recommended that the present system of iron secondary standards be extended further into the ultra-violet, since there are no modern measurements extending below about λ 3300. A list of wave-lengths computed from the standards adopted in 1928 in the less refrangible parts of the spectrum was given, which indicated that all the older measurements in this part of the spectrum were considerably in error, being over one part in one million too great. Accordingly I decided to measure a set of lines in the region λ 2300 to λ 3100 by means of the usual interferometer method. It was found that the measures agreed very well with the computed I.A.U. wave-lengths, the systematic difference being practically nil, while the mean accidental difference was less than 0.001 Å.

The wave-lengths also agreed very well with those determined recently by Burns in the vacuum iron arc spectrum; indeed, almost as well as they did with the I.A.U. computed values, although my values showed a very small ($J - B = +0.0002$ Å.) systematic difference from Burns. The difference can be attributed to a pressure shift since it is about the amount to be expected for stable lines in this region, but it is too small to have any very great significance. The agreement with Burns's 1930 revision of his 1913 interpolated measures was also fairly satisfactory, particularly from the absence of systematic difference, although the accidental differences were rather greater. There is however, considerable disagreement with all the old interpolated measurements which are based on Buisson and Fabry's standards and also with Buisson and Fabry's measurements.

At the same meeting of the International Astronomical Union, it was also decided to make a radical change in the values of the iron lines adopted in 1925, all wave-lengths from λ 3370 to λ 5506 being reduced by about one part in 2 million. This is particularly impressive on account of the excellent agreement of the older determination among themselves, but seems to be fully justified. However, a few iron lines in the region λ 4000 to λ 4400 were measured and found to be in almost perfect agreement with the values adopted

by the I.A.U. in 1928, indicating that my apparatus is apparently free from the cause which brought about the systematic errors in the work of the earlier observers.

In addition to the iron lines, a few lines were measured in the ultra-violet part of the mercury spectrum.

Experimental.

The wave-lengths were measured by means of the Fabry and Perot interferometer, the fixed or étalon type being used. Four separating rings of fused silica of thicknesses $1\frac{1}{4}$, $2\frac{1}{2}$, 5 and 10 mm. were used. The measurements obtained with the $1\frac{1}{4}$ and $2\frac{1}{2}$ mm. étalons were made primarily for finding the phase correction, but it was found that the measurements made with the $2\frac{1}{2}$ mm. étalon gave a useful check on the values found with larger étalons, and they were included in the means, being given half weight.

In photographing the interference rings, exposures were usually made in the order (Cd or Ne) — (Fe) — (Cd or Ne) in order to detect any change in the optical thickness of the étalon during exposure.

Now it is not possible to photograph the red standard and an iron line at, say, λ 2500 on the same setting of a spectrograph which gives sufficiently great dispersion and takes a plate of reasonable size. It was therefore essential to be able to set the spectrograph for the red and then for the ultra-violet and again for the red by scale sufficiently accurately to avoid the necessity of making focus plates. A Hilger E(1) spectrograph was chosen and was found to be perfectly satisfactory in this respect. In the region 3100 to 2300 a quartz prism was used and was found to give quite adequate dispersion, the mean dispersion over this range being about 3.5 Å. per millimetre. The slit width was 0.1 mm.

The spectrograph was very rapid; for example, using platinum sputtered plates in the étalon, typical exposure times were: neon, 3 minutes; iron (ultra-violet), 5 minutes; iron (visible), 20 seconds. The exposure for the Cd red line, using the approved type of Michelson tube, was about 20 minutes, and since the plates taken with neon standards gave no systematic difference in the iron wave-lengths when compared with those taken with the primary standard, it was thought preferable to use neon for most of the plates since the much shorter exposure required greatly reduced the risk of change of length of the étalon during exposure. The neon radiation was obtained from a Hilger G.E.C. neon lamp, which was worked directly off the 200-volt mains.

Two quartz-fluorite objectives were used for projecting the rings; these had focal lengths of 6 inches and 12 inches and were constructed by Adam Hilger,

Ltd. They both gave very fine definition and were so well corrected for achromatism (the difference f 6000 and f 2500 being less than $\frac{1}{2}$ mm.), that it was quite unnecessary to alter the focus when changing from the red to the ultra-violet part of the spectrum.

The étalon plates, which were of crystalline quartz, were made by Hilger, and were chosen from four different pairs by testing them with mercury vapour light when set up with a $2\frac{1}{2}$ mm. separator. The central $1\frac{1}{2}$ cm. of them was so flat that when the plates were set parallel it was impossible to notice any change in the size of the interference ring as one moved from one part to another. In actual practice a $\frac{1}{2}$ -cm. circular diaphragm was placed immediately in front of the étalon.

The étalon was placed at such a distance from the objective of the rings, that a real image of the diaphragm was projected on to the prism of the spectrograph, since this ensures that the same portion of the étalon plates is used for the two spectra being compared. A few plates were taken with the étalon and its diaphragm close to the objective of the rings, so that a real image of the diaphragm was not formed on the prism, but no systematic difference between the wave-lengths found from these plates and those found from plates with the étalon in the correct position could be detected.

The image of the light source was projected on the diaphragm by means of either a quartz-fluorite lens or a single quartz lens of 6-inch focus; when the single quartz lens was used it was focussed for the middle of the region being photographed, and no trouble was experienced from lack of achromatism. The image was a five-fold magnification of the source, and in the case of iron, surplus radiation, particularly that from the poles, was prevented from falling on the étalon mount. The diaphragm was made of polished brass, so that heat radiation falling on it would be reflected away as much as possible.

The étalon was carried by a mount which also held the quartz-fluorite achromat. It was very convenient to use, the rings being centred on the slit by simply adjusting two screws while the objective was focussed by means of a helical mount.

Great care was taken in aligning accurately, the light source, condenser, étalon, objective of the rings, and spectrograph.

For most of the work Ilford special rapid process panchromatic plates were used, but for a few of the plates Ilford soft gradation plates were used on account of their greater rapidity, particularly in the red. The total time of exposure was *only* about 8 minutes when photographing the visible iron lines and 12 minutes for the ultra-violet, including the two neon exposures, and as a

result very few plates had to be discarded on account of change of length of the étalon during the first and second neon exposures. Plates which showed a difference of more than 1/500th of a fringe were not used for measurement.

The iron arc used was of the type recommended by the International Astronomical Union in 1928, the negative pole, an iron rod of about 7 mm. diameter, being placed on top, while the positive pole consisted of an iron oxide bead resting on an iron support of about 2 cm. diameter. The upper pole was cooled by means of a large iron bush, and was always kept free from drops of iron oxide. The arc was burnt with a current of $3\frac{1}{2}$ to 4 amperes and varied in length between $1\frac{1}{2}$ and 2 cm. The central 1 mm. was projected on to the étalon.

The étalons were adjusted by the light from a Cooper-Hewitt mercury vapour lamp. This was run with half the normal current, since the light under these conditions was quite adequate and the lines were sharper than when the full current was used. The plates were inspected for parallelism before each exposure although they remained parallel for a very much longer time than that usually intervening between two exposures. As is now well known, the penetration of the reflecting films of the interferometer is different for different wave-lengths of light and it is therefore necessary to find the correction to be applied to the apparent wave-lengths of lines found with an étalon. This correction is known as the phase correction. The most convenient way of determining it, is to measure the apparent wave-lengths of a line with two or more different thicknesses of étalon; the correction may then be directly determined, being given by the formula

$$c = \frac{t_1(\lambda_2 - \lambda_1)}{t_2 - t_1} \times \frac{t_2}{t_1}, \quad (1)$$

where c is the correction for an étalon of thickness t and λ_1 and λ_2 are the uncorrected wave-lengths given by étalons of thicknesses t_1 and t_2 respectively. The correction was found by measuring the wave-lengths of iron, neon and mercury lines with étalons of thicknesses ranging from $1\frac{1}{2}$ to 10 mm. The neon and mercury lines were measured because they gave sharper fringes than even the best iron lines, especially with the 10 mm. étalon. In order to avoid systematic errors, a large number of plates, on which a comparatively small number of lines were measured, were taken for this purpose. The phase correction for the platinum sputtered plates was quite small, being only -0.004 A. at λ 3000 for the $\frac{1}{2}$ -cm. étalon. For the 1-cm. étalon it was half this quantity, and for the $\frac{1}{4}$ -cm. étalon, double. At λ 2300 it was -0.007 A. for the $\frac{1}{2}$ -cm. étalon.

The Measurements.

The plates were measured with the aid of a Hilger photo-measuring micrometer, three or four settings being made on each ring segment. Two or three, or occasionally four, rings of each system were measured and from these data it was possible to calculate e , the fractional part of the order of interference at the centre of the ring system, without any knowledge of the absolute angular scale of the plates. For we have

$$a + e = n_k^2 / (n_{k+1+a}^2 - n_k^2), \quad (2)$$

where n_k is the diameter of the k th ring and n_{k+1+a} is the diameter of the n_{k+1+a} th ring.

Only the diameters of the two innermost rings were used for the evaluation of the numerator of the expression (2), but the diameters of the outer rings were used in evaluating the denominator. In order to reduce the effect of accidental errors in the measurement of the ring diameters, the denominators were plotted on graph paper against the wave-lengths and a smooth curve was drawn through them. In evaluating the fractional value, the denominator read from the curve was used, but it only differed by a very small amount from that given by the mean of the direct measurements of a single ring system except in the case of a few diffuse lines where it occasionally differed by as much as 1 or 2 per cent. It was gratifying that throughout the course of the work no systematic difference between the fractions yielded by the first and those yielded by the second rings was detected.

The advantage of this method of reduction is that it is not necessary for the spectrograph to give the same magnification of the slit over the whole range of the plate, and it is not necessary even to know how great this magnification is. It is only necessary that there be no distortion of the ring system of any given line. The spectrograph and the objective of the rings were tested for this point and found to be quite satisfactory, as was to be expected from the fact that there was no systematic difference between the values of the fractional order of interference given by the first and second rings.

In addition to knowing the fractional order of interference it is necessary to know the whole number, p , of the order of interference, since the wave-length of the line is given by the relation,

$$\lambda = \frac{2t}{p + e}. \quad (3)$$

In the case of all the iron lines measured above λ 2400, p was found from the

wave-lengths given by Burns,* which were quite accurate enough for the purpose. Below λ 2400 the wave-lengths were taken from Kayser's 'Handbuch der Spectroscopie,' vol. 7.

The thickness of the étalon was measured in terms of the neon secondary standards or occasionally the red cadmium line. On account of the great homogeneity of the radiations from these sources and the high reflecting power of metallic films for red light, it was possible to measure the rings to within one- or two-thousandths of a fringe.

In estimating the accuracy of measurements, it is perhaps advisable to differentiate between systematic and accidental errors. In the present work the systematic errors of the plates were found by taking the mean of a number, about 20, of the sharper iron lines which had been measured on all the plates covering the particular region of the spectrum. If there were no systematic errors on the plates, the residuals between the mean wave-lengths and those of any one plate would be algebraically zero. Actually this was not the case, but the residuals were quite small, being in only one case as great as 0.001 Å.; the mean value of a residual was 0.0003 Å., or 1 part in 10 million. The plates were reduced to the mean by adding or subtracting the residual in order to reduce the systematic errors of lines which had been measured on only a small number of plates, but since the mean residual was only 0.0003 Å. the effect on the final wave-length was usually only of the order of one or two ten-thousandths of an angstrom.

A few of the lines were measured on plates which were considerably over-exposed or considerably under-exposed as well as on correctly exposed plates, but even a very large error in exposure appeared to make no difference to the wave-lengths obtained, although it naturally made the measurement of the plate more difficult.

The accidental errors were considerably greater than the systematic errors. As can be seen from Table I, which gives the wave-lengths obtained from different plates for a number of lines distributed throughout the spectrum, the mean accidental error for a single measurement was about 0.001 Å. Since most of the lines were measured on a fairly large number of plates it might have been considered reasonable to retain the fourth decimal place of the wave-lengths (all the calculations were made to eight figures), but this was considered inadvisable partly on account of the thickness of the iron lines. It was found that even the best iron lines gave measurable fringes with paths of interference

* 'Z. Wiss. Phot.,' vol. 12, p. 203 (1913).

of not much greater than about 60,000 waves, which means that $\lambda/\delta\lambda$ for the lines is probably about 120,000. The temperature thickness of iron arc lines alone is probably such that $\lambda/\delta\lambda = 150,000$ or at most 200,000. Now it seems meaningless to define the wave-length of a line to much less than about one-twentieth of its thickness, *i.e.*, about 0.001 Å, especially in view of the possibility of hyperfine structure occurring in the iron lines. Further, although all the wave-lengths were reduced to N.T.P., by means of tables constructed from the data on the refractive index of air determined at the Bureau of Standards,* it was not possible to make any correction for the humidity of the air, as there are at present no data on this point. It is a well-known fact that actual errors are nearly always greater than the calculated probable errors, and accordingly it was decided not to retain the fourth decimal place for the wave-lengths of the iron lines. In any case it is very doubtful if a fourth figure after the decimal place would be of any advantage, as the measurements are intended for standards for the interpolation of wave-lengths, for which purpose a fourth figure after the decimal place is probably of no practical value.

The lines selected for measurement were chosen so that if possible there were no gaps of much more than about 10 Å. between them, and naturally those which gave the sharpest interference fringes were given preference. It is interesting that this criterion automatically eliminated all the lines (about 50) stated by Lang† to be unsuitable as standards on account of the great differences in wave-length shown by them according to the character of the iron arc in which they are observed. Most of the lines in this region recommended for further observation by the I.A.U. in 1928‡ were measured. Preference was also given to lines which were easily identified on maps of the iron arc spectrum, since standards which are easily recognised save a considerable amount of time and trouble in making measurements by interpolation.

It has been suggested that the lines below about λ 3300 Å. in the iron arc in air spectrum are not suitable for use as wave-length standards, on account of their not being accurately reproducible, but the results of the present investigation appear definitely to disprove this idea, as can be seen from the data given in Table I, and the excellent agreement of the observed values with the values calculated from terms derived from the wave-lengths adopted in 1928 by the I.A.U. The agreement with Burns's§ recent measurements of

* Meggers and Peters, 'Sci. Papers Bur. Stds.,' No. 327 (1918).

† 'Z. Wiss. Phot.,' vol. 15, p. 223-292 (1915).

‡ 'Trans. I.A.U.,' vol. 3 (1928).

• § Burns and Walters, *loc. cit.*

the vacuum iron arc is also very satisfactory, the mean accidental difference being only ± 0.001 A. while the systematic difference is less than one-quarter of this amount.

Description of Tables.

Table I gives the wave-lengths obtained from different plates for a number of lines evenly distributed throughout the range investigated.

Table II gives the wave-lengths found in the present investigation for ten lines in the visible part of the iron spectrum, together with the values recommended by the I.A.U. in 1928, and those found by Babcock, by Burns and by Monk.

Table III contains the wave-lengths of five lines in the ultra-violet part of the spectrum of mercury, which were measured in connection with the determination of the phase correction of the interferometer plates. Under N is given the number of plates on which the line was measured.

Table IV contains the wave-lengths of 68 lines in the ultra-violet part of the spectrum of the iron arc in air. The first column gives the wave-lengths determined in the present investigation, and the second gives the numbers of plates on which the lines were measured. The third column gives the wave-lengths of the lines in the vacuum arc, determined by Burns and Walters; a letter *c* placed after a line denotes that the wave-length was computed, not measured. The fourth column gives the computed values given by the I.A.U. in 1928. The fifth column gives Burns's corrected values of his 1913 grating measurements. The sixth column gives the interferometric determinations of Buisson and Fabry. The seventh column gives the 1915 interferometric wave-lengths of Burns. The eighth column gives the wave-lengths calculated by the author from the term data collected by Miss Moore and H. N. Russell. The adopted term values for all the final states were those given by Babcock, while the values for the initial states were either those of Babcock, Laporte, Walters, or Meggers; these are denoted by B, L, W and M respectively. The ninth column gives the classification of the lines. The notation of Burns and Walters has been used. The tenth column gives the wave-number calculated from my eight figure wave-lengths.

Table I.

3091·579	2987·291	2832·436	2584·535	2410·517
·577	·291	·435	·534	·516
·578	·291	·435	·533	·516
·578	·292	·435	·535	·515
·579	·292	·437	·536	·518
·579	·292	·438	·534	·517
·577	·290	·436	·535	·518
·579	·289	·438	·533	·517
·579	—	·436	·535	·518
·580	—	·435	—	—
·580	—	—	—	—
·579	—	—	—	—

Table II.

Jackson.	I.A.U., 1928.	Revised interpolated.	Babcock, 1927.	Burns, 1928.	Monk.
4045·815	·815	·816	·814	·815	—
4063·597	—	—	·597	—	—
4071·740	—	—	·741	—	—
4202·033	·031	·031	·032	·031	—
4280·479	—	—	·480	—	—
4307·906	·906	·907	·906	·904	—
4325·766	·765	·764	·765	·765	·765
4383·547	·547	·548	·548	·546	·548
4404·752	·752	·752	—	·752	—
4415·124	·125	·126	·125	·124	—

Table III (Mercury).

—	N.	—	N.
2652·042	5	3021·497	6
2893·596	6	3125·668	4
2967·638	5		

Table IV.

Jackson.	N.	Burns's vacuum arc, 1930.	I. A. U. com- puted.	Burns's cor- rected 1913 values.	Buisson and Fabry.	Burns's 1915 interfero- metric.	Com- puted.	Classification.	Wave- number (Jackson).
2327.392	3	—	—	—	—	—	—	—	42953.362
31.305	3	—	—	—	—	—	—	—	881.250
32.795	3	—	—	—	—	—	—	—	853.865
37.002	2	—	—	—	—	—	—	—	776.726
59.102	3	—	—	—	—	—	—	—	376.036
64.825	4	—	—	—	—	—	—	—	273.482
79.273	3	—	—	—	—	—	—	—	016.817
80.757	3	—	—	—	—	—	—	—	41990.624
88.625	2	—	—	—	—	—	—	—	852.317
2399.238	5	—	—	—	—	—	—	—	667.201
2406.657	3	—	—	—	—	—	—	—	536.424
10.517	8	—	—	—	—	—	—	—	472.252
11.066	7	—	—	—	—	—	—	—	462.810
13.309	10	—	—	—	310	—	—	—	41424.456
47.708	5	.707c	—	—	—	—	.709 B	$a^5 D_4 - c^5 F_3^*$	40842.172
57.595	8	—	—	—	—	—	—	—	677.869
65.148	8	—	—	—	—	—	—	—	553.257
68.879	7	—	—	—	—	—	—	—	491.968
74.814	8	—	—	—	—	—	—	—	394.876
2496.533	8	—	—	—	—	—	—	—	40043.476
2507.900	7	—	—	—	—	—	—	—	39861.998
16.114	2	—	—	—	—	—	—	—	731.875
29.833	2	.832c	—	—	—	—	.833 B	$a^5 D_1 - c^5 D_1^*$	516.418
30.692	1	—	—	—	—	—	—	—	503.013
42.102	2	—	—	—	—	—	—	—	327.270
62.534	8	—	—	—	541	—	—	—	38912.184
84.535	8	.535c	—	—	—	—	.541 W	$a^5 F_5 - c^5 G_3$	680.121
85.876	10	—	—	—	—	—	—	—	659.940
2598.369	9	—	—	—	—	—	—	—	474.664
2611.872	3	—	—	—	—	—	—	—	375.294
13.822	2	—	—	—	—	—	—	—	246.753
25.668	5	—	—	—	—	—	—	—	074.198
28.292	3	—	—	—	296	—	—	—	38036.188
35.807	8	.808c	—	—	—	—	.810 W	$a^5 F_3 - b^5 G_5^*$	37927.752
44.005	7	—	—	—	—	—	—	—	810.169
79.063	9	—	—	—	065	—	—	—	314.025
89.212	7	—	—	—	—	—	—	—	174.589
2699.108	8	—	—	—	—	—	—	—	37038.301
2723.577	2	.576c	—	—	—	—	.576 B	$a^5 D_3 - b^5 P_1^*$	26705.568
35.476	5	.473c	—	—	—	—	.473 B	$a^5 F_4 - d^5 D_5^*$	545.909
67.525	9	.523	—	.518	—	—	.521 B	$a^5 F_4 - d^5 D_4^*$	122.722
72.109	2	.108c	—	.112	—	—	.108 B	$a^5 D_3 - b^5 P_3^*$	36062.986
2776.230	10	.223	—	.226	.225	—	.223 L	$a^5 F_3 - b^5 G_3^*$	35983.667
2804.531	5	.522	—	.523	—	—	.521 L	$a^5 F_4 - b^5 G_4^*$	646.233
06.985	8	—	—	.985	—	—	—	—	614.938

Table IV—(continued).

Jackson.	N.	Burns's vacuum arc, 1930.	I.A.U. com- puted.	Burns's cor- rected 1913 values.	Buisson and Fabry.	Burns's 1915 interfero- metric.	Com- puted.	Classification.	Wave- number (Jackson).
13·288	9	·289	—	·288	·290	—	·289 L	$a^5 F_1 - b^5 G_1^*$	535·159
23·276	3	·277	—	·276	—	—	—	—	409·447
32·436	10	·436	—	·433	—	—	·436 L	$a^5 F_3 - b^5 G_1^*$	294·940
38·120	7	·120	—	·118	—	—	·123 L	$a^5 F_3 - b^5 G_1^*$	224·262
51·797	11	·798	—	·798	·800	·802	·799 L	$a^5 F_1 - b^5 G_1^*$	35055·336
2869·307	8	·305	—	·311	—	—	·307 B	$a^5 D_3 - a^5 G_1^*$	34341·414
2912·158	11	·159	·158	·159	·157	—	·158 B	$a^5 D_3 - b^5 F_3^*$	328·771
29·008	10	·007	·007	·004	—	—	·007 B	$a^5 D_3 - b^5 F_3^*$	34131·291
41·343	2	·343	·342	·341	·347	·348	·343 B	$a^5 D_3 - b^5 F_3^*$	33988·162
53·940	8	·940	·940	·941	—	—	·940 B	$a^5 D_3 - b^5 F_3^*$	843·229
57·365	9	·365	—	·368	—	—	·365 B	$a^5 D_1 - b^5 F_1^*$	804·307
65·255	10	·254 _c	—	·256	—	—	·254 B	$a^5 D_0 - b^5 F_1^*$	714·100
81·446	8	·448	—	·446	—	—	·445 W	$a^5 D_3 - a^5 F_3^*$	531·012
87·291	9	·292	—	·291	·293	·298	·289 M	$a^5 F_4 - c^5 F_3^*$	465·410
2999·513	7	·510	—	·514	—	·518	·517 M	$a^5 F_4 - c^5 F_3^*$	83329·062
3037·387	3	·389	·389	·389	—	—	·388 B	$a^5 D_1 - b^5 D_3^*$	32913·488
47·605	2	·605	·605	·605	—	—	·605 B	$a^5 D_3 - b^5 D_3^*$	803·138
57·447	9	·445	·448	·447	—	—	·447 B	$a^5 F_3 - c^5 D_3^*$	697·550
59·085	2	·085	·086	·086	—	—	·086 B	$a^5 D_3 - b^5 D_3^*$	680·054
67·245	10	·245	·245	·246	—	—	·245 B	$a^5 F_4 - c^5 D_3^*$	593·103
75·722	9	·720	·719	·722	·725	·726	·720 B	$a^5 F_3 - c^5 D_3^*$	503·280
83·743	12	·741	·742	·742	—	·747	·742 B	$a^5 F_3 - c^5 D_3^*$	418·739
91·579	12	·577	·577	·578	—	·582	·578 B	$a^5 F_1 - c^5 D_3^*$	336·572

Comparison with other Measurements.

(a) In the case of the lines measured in the visible part of the spectrum, it is interesting to compare the values found in this investigation with those adopted by the International Astronomical Union in 1928,* and accordingly these values are given in the second column of Table II. The agreement is almost as perfect as could be expected, since the mean systematic difference (J — I.A.) is only + 0·0003 Å., while the mean accidental difference is $\pm$ 0·0006 Å.; the agreement with Babcock's measurements† is almost equally satisfactory, the mean systematic difference (J — B) being — 0·0001 Å., while the mean accidental difference is $\pm$ 0·0008 Å.; as also is that with Burns's latest measurements,‡ the mean systematic difference (J — B) being + 0·0008 Å., while the mean accidental difference is $\pm$ 0·0006 Å.

* 'Trans. I.A.U.,' vol. 3 (1928).

† 'Astrophys. J.,' vol. 62, p. 375 (1927).

‡ 'Trans. I.A.U.,' vol. 3 (1928).

In the case of the revised interpolated wave-lengths the mean systematic difference ($J - R.I.$) is only $-0.0001 \text{ \AA}$., but the mean accidental difference is rather greater, being $\pm 0.0012 \text{ \AA}$.. Unfortunately, only two of the lines in my list were measured by Monk,* but the agreement is quite good, the systematic difference being nil, while the mean accidental difference is $\pm 0.001 \text{ \AA}$.

The measurements of these lines in the visible were carried out mainly with the object of ascertaining whether my apparatus and method would give results in accordance with those found by the observers on whose results the I.A.U. standards of 1928 were based, and seem to show quite definitely on account of the very low values of the systematic differences, that this is the case. This is very satisfactory, especially in view of the change made by the wave-length committee in 1928. This consisted in reducing the older values adopted in 1925 by about $0.002 \text{ \AA}$., in this region, and although the change is almost certainly entirely justifiable, the agreement of the older values among themselves was surprisingly good, and it is very difficult to understand how so great a systematic error arose. The fact that my results are in almost perfect accord with the more recent measurements, and disagree with the older ones, shows that my apparatus is free from the source of error affecting the earlier values, and also gives a certain amount of confirmatory evidence in justification of the system of standards adopted in 1928. The difference between these values and the earlier ones was caused partly by the change in the specification of the arc (in the older work, the arc used was too short to be entirely free from pole effect), but this cause alone could not have been responsible for the whole difference, since even the stable lines were affected.

(b) In the ultra-violet below $\lambda 3300$ there are at present no secondary standards of iron adopted by the I.A.U., because up till now no suitable measurements have been made in this region. The only interferometric measurements of the iron arc in air which extend well into the ultra-violet are those of Buisson and Fabry,† and a set of measurements by Burns to which reference will be made below. They were both carried out with short arcs which were probably influenced by pole effect, and are therefore not strictly comparable with my measurements.

Recently, however, Burns and Walters‡ have carried out a very extensive investigation of the spectrum of the iron arc *in vacuo*, including very accurate

* 'Astrophys. J.', vol. 62, p. 375 (1925).

† 'Astrophys. J.', vol. 28, p. 169 (1908).

‡ 'Pub. Alleghany Obs.', vol. 6, No. 11.

interferometric measurements, which are undoubtedly free from pole effect. On account of the pressure shift, lines measured in the arc *in vacuo* should have a slightly shorter wave-length than the same lines in the arc in air, but in the region below λ 3100 this difference becomes almost negligibly small. Assuming that the shift is proportional to the cube of the wave-length, which appears to be fairly definitely established, the shift at λ 2800 would be expected to be only about 0.0006 Å., for group *b* lines. It is therefore probable that my measurements are more comparable with those of Burns and Walters than with the older ones. That this is the case can be seen at once from Table IV, from which it can be seen that the mean accidental difference is ± 0.001 Å., while the mean systematic difference ($J - B$) is only $+ 0.0003$ Å. This difference is of the sign to be expected from the pressure shift, although it is possibly slightly smaller than might have been expected. However, this agreement is very satisfactory, and it is interesting to note that the agreement with the computed wave-lengths of Burns and Walters is nearly as good as that with their observed values.

The agreement with the computed values for the arc in air given by the I.A.U. in 1928* is also very satisfactory, the mean accidental difference being ± 0.001 Å., while the mean systematic difference ($J - \text{I.A. comp.}$) is $+ 0.0003$ Å.; or, if the line λ 3075.72 is neglected, nil. This means that there is no systematic difference greater than that to be expected from the accidental differences.

The measurements of Buisson and Fabry have been given in Table IV since they are the only previous interferometric determinations of wave-length which extend well into the ultra-violet. It is immediately evident that there is a systematic difference between the values of Buisson and Fabry and those found in the present investigation, the mean value of this difference for eleven lines in the region λ 2400 to λ 3100 being ($J - B$ and F) = $- 0.003$ Å. At most 0.001 Å. can be attributed to difference in the type of arc used in the two investigations, since only stable lines were measured, and the remaining 0.002 Å. must be attributed to experimental error. Now it is thought that the systematic error of the wave-lengths found in the present investigation is probably not greater than ± 0.0005 Å., and this is supported by the agreement with the I.A.U. computed values and with the recent work of Burns and Walters. If this is the case, there must be an experimental error of the order of 0.002 Å. in the measurements of Buisson and Fabry. Considering that their measurements were made with only one thickness of étalon, a short one of $2\frac{1}{2}$ mm., it

* 'Trans. I.A.U.,' vol. 3 (1928).

is not very surprising that an error of this magnitude should arise, particularly in the region λ 2400 to λ 3100 where the phase correction is relatively large with so short an interference path. The mean accidental difference is ± 0.0035 Å. The number of lines measured both by Buisson and Fabry and by the author is rather small, being only 11, but a comparison with the interpolated measurements of Burns* for which Buisson and Fabry's standards were used shows that it is not possible to correct them by a simple linear correction. For instance, at λ 2500 the difference is about 0.006 Å., at λ 2600 it has risen to 0.012 Å., at λ 2800 it is almost zero, while at λ 3000 it is only about 0.003 Å. A similar conclusion results from a comparison with the interpolated measurements of Lang (*loc. cit.*), and it is therefore desirable that as soon as a system of secondary standards is available in this region, new interpolated measurements be made.

In 1915 Burns† carried out measurements of a number of lines in the iron arc spectrum between λ 2800 and λ 3500, using the nickered interferometer plates which had previously been used by Buisson and Fabry. These wave-lengths, however, do not agree with the values found in the present investigation, or with the calculated values of the I.A.U., or with those of Burns and Walters for the vacuum arc. In the range λ 2900 to λ 3100 there is a systematic difference $(J - B) = -0.005$ Å., but apart from this the mean accidental difference is only ± 0.001 Å., although the observations were made with a short iron arc. This systematic difference is surprisingly great in view of the small value of the mean accidental difference, and is probably due to the use of incorrect values for the phase correction, although the use of a shorter arc may be responsible for part of it. In a private communication Dr. Burns agrees with these conclusions and considers that the small systematic correction of -0.005 Å. is justified. It is interesting that the revised values of the 1913 interpolated measurements of Burns, which appear in the eighth column of Table I of Burns and Walters' paper on the spectrum of iron vacuum arc, lead to exactly the same value for the correction. This was to be expected, since the systematic difference between these values and those found in the present investigation is only $(J - B) = -0.0001$ Å., while, excluding $\lambda\lambda$ 2767 and 2778, the mean accidental difference is ± 0.001 Å.

Two of the lines, $\lambda\lambda$ 3075 and 3083, occurring in my list have been measured recently by Pressentin,‡ whose values are respectively 0.006 Å. and 0.004 Å.

* Burns, 'Z. Wiss. Phot.', vol. 12, p. 207 (1913).

† 'Sci. Papers Bur. Stds.' No. 251 (1915).

‡ 'Z. Physik,' vol. 60, pp. 125-136 (1930).

higher than mine. This discrepancy is very great, but no explanation can be offered for it. Pressentin's wave-lengths appear to be systematically too high, the error decreasing, approximately linearly, from about 0.005 Å. at λ 3100 to nil at λ 3500, when they are compared with the best other values now available.

It is possible to calculate the wave-lengths of some of the iron lines from the levels given by Miss Moore and Russell.* A considerable number of these levels were derived by Babcock from his interferometric measurements of iron, and should be very accurate. As can be seen from Table IV, the agreement between my observed wave-lengths and those calculated from Babcock's levels is very satisfactory, the mean systematic difference ($J - B$ calc.) being only + 0.0002 Å. while the mean accidental difference is ± 0.001 Å. The wave-lengths of lines involving levels not determined by Babcock have also been computed, but the agreement is naturally not so good and the values are printed in italics.

Summary.

Ten lines in the spectrum of the iron arc in air, between λ 4000 and λ 4400, have been measured by interferometric comparison with the red line of cadmium or with the secondary standards of neon. The results are found to be in almost perfect agreement with the wave-lengths recommended by the I.A.U. in 1928, the mean systematic difference ($J - I.A.$) being only + 0.0003 Å., while the mean accidental difference is ± 0.0006 Å.

Sixty-eight lines in the spectrum of the iron arc in air between λ 2300 and λ 3100, have also been measured interferometrically. These agree well with the vacuum arc measurements of Burns and Walters, but, as is to be expected on account of the pressure shift, they are slightly greater in wave-length, the mean systematic difference being 0.0003 Å., while the mean accidental difference is ± 0.001 Å. The agreement with the computed values for the arc in air given by the I.A.U. in 1928 is equally satisfactory, and that with certain wave-lengths calculated by the author from energy levels given by Babcock is also very satisfactory. The measurements above λ 2800 agree very well with Burns's interpolated values of 1913 when the latter are corrected by means of the table given recently by Burns.†

Five lines of mercury in the ultra-violet have also been measured.

* 'Astrophys. J.,' vol. 68, pp. 151-164 (1928).

† 'Pub. Alleghany Obs.,' vol. 8, No. 1. [Note added in proof.—Dr. Burns, while this paper was in proof, has sent me a list of iron lines down to λ 2200, which he and Dr. Walters have measured in the vacuum arc. This list includes nearly all the lines I have measured and the agreement is very good; the mean accidental difference being ± 0.001 Å, while the mean systematic difference ($J - B. \& W.$) is + 0.0002 Å.]

In conclusion, it is a great pleasure to thank Prof. A. Fowler for his great interest and encouragement throughout the course of the work, and to express my gratitude to Dr. Burns for the suggestion that I should use Babcock's levels for calculating the wave-lengths of many of the lines which I had observed.

The Photo-Elastic Dispersion of Vitreous Silica.

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1. The dispersion of the double refraction induced by stress in isotropic transparent substances has been the subject of a number of investigations.* All of these, however, have dealt with compound substances, such as ordinary glasses and nitro-cellulose. It appeared of interest to obtain data, as accurate as possible, for a substance of glassy type, containing only a single chemical constituent, and in which the complications arising from progressive creep (such as occurs in nitro-cellulose and gelatine) were absent. Vitreous silica provides such a material and is now obtainable in fair-sized blocks of good optical quality.

2. Two rectangular blocks of vitreous silica were obtained from the Thermal Syndicate, Ltd. Their dimensions were as follows: a (the height) being parallel to the line of stress, b (the breadth) being at right angles to both the line of stress and the rays of light, and d (the thickness) being in the direction of travel of the light through the block:—

$$\text{A. } a = 2.142, \quad b = 0.467, \quad d = 0.902.$$

$$\text{B. } a = 4.270, \quad b = 1.228, \quad d = 3.250.$$

All the measurements being in centimetres.

Owing to the peculiar opacity of vitreous silica when slowly cooled, it was

* Macé de Lépinay, 'C. R.,' vol. 86, p. 326 (1878); F. Pockels, 'Ann. Physik,' ser. IV, vol. 7, pp. 745, *et seq.* (1902); L. N. G. Filon, 'Proc. Camb. Phil. Soc.,' vol. 11, pp. 478-492 (1902), and vol. 12, pp. 55-64 and 313-336 (1903); 'Phil. Trans.,' A, vol. 207, pp. 263-306 (1907); 'Proc. Roy. Soc.,' A, vol. 83, pp. 572-579 (1910); S. R. Savur, 'Proc. Roy. Soc.,' A, vol. 109, pp. 338-350 (1925).

impossible to anneal the specimens. On the whole these were remarkably free from initial double-refraction. In the earlier experiments (on specimen A) a slight effective residual stress, parallel to the dimension a , was found to exist, and allowed for in the reductions. The method used in the later experiments eliminated such an effect automatically.

The faces $a \times b$ of each block were polished.

The specimen A and, to a much lesser extent, B, showed a certain amount of striation in the internal structure.

3. The stress was applied by means of a lever and weight, the apparatus being sensibly identical with that described by Filon and Jessop,* to whose paper the reader is referred.

The method of measurement of the stress-optical coefficient C (the difference per unit stress of the indices of refraction for light polarised in and perpendicular to the line of stress) was identical in principle with the spectrometer method described by Filon,† but originally used in a somewhat different form by Mach.‡

An important modification was introduced, which greatly increased the accuracy of the method. After the light had passed through a polariser, the strained specimen, and an analyser, the axes of the polariser and analyser being crossed and at 45° to the line of stress, it was focussed by a lens upon the slit of a spectroscope, the slit and the mid-plane of the specimen being in conjugate planes of the lens, and the distances so adjusted that a much enlarged image of the specimen was formed in the plane of the slit. This ensured that the light entering the slit had all passed through a narrowly limited region of the specimen, and thus eliminated largely the effect of lack of homogeneity shown by striation. Further, lateral adjustment of the lens allowed the same part of the image of the specimen to be brought accurately upon the slit. By this device it has been possible to apply the spectrometer method to measure C in materials such as bakelite, which show considerable "residual stress" varying rapidly from point to point.

The image was also used to check the centering of the load and the consequent uniformity of stress in the middle part of the specimen, by making visible, without disturbance of the apparatus, any lack of uniformity in the colour of the image at the tints of passage.

The effect of the above optical arrangement is to reduce considerably the proportion of light which enters the slit. In order to overcome this difficulty

* 'Phil. Trans.,' A, vol. 223, pp. 90, 91 (1922).

† 'Camb. Phil. Soc. Proc.,' vol. 12, pp. 55, *et seq.* (1902).

‡ Ernst Mach, 'Ann. Physik,' vol. 146, pp. 313-316 (1872).

a source of high intensity was used, viz., an arc lamp in the earlier experiments, and a 500 candle-power Pointolite lamp in the later ones.

4. If $\tau(\lambda)$ is the retardation produced by the specimen in light of wave-length λ , the spectrum observed is crossed by dark bands, whose centres are given by the equation

$$\tau(\lambda) = n\lambda, \quad (1)$$

n being an integer. The object of the experiment is to determine the form of $\tau(\lambda)$.

Although the total extinction of the light is given by equation (1), appreciable partial extinction is produced for neighbouring values of λ , so that the dark bands which cross the spectrum have a quite considerable breadth. For high orders, however, the successive values of λ which give the centres of the bands are fairly close, so that the breadth of the bands is much smaller and settings on individual bands can be made with accuracy. On the other hand, any error in λ is multiplied by the order of the band, so that the gain in accuracy of setting may be more than balanced by the increase in the multiplying factor when it comes to the determination of τ . There are, however, certain decisive advantages in working with a high order; these will be explained later, in § 15. It is also essential if the dispersion of the spectrometer is considerable.

For the 1924 observations here described an ordinary one-prism (60°) spectroscope, with graduated circle, was employed; for the 1930 observations it was replaced by a Littrow spectroscope of length 3 feet 9 inches, giving a much higher dispersion.

The calibration of the spectrometer was in every case carried out by means of a comparison spectrum, obtained in the earlier experiments from the glowing gas between cored carbons containing a calcium filling; later from the arc between iron poles.

5. The first set of observations was taken on specimen A.

This specimen was loaded until the bands of the first, second, and third orders, successively, appeared at the violet end and travelled through the spectrum; the third order band could not be obtained beyond λ 4700, owing to the approach to the breaking stress of the material. The wave-lengths λ of the centres of the bands were measured with the spectrometer, and, on multiplying by the order n of the band, $\tau(\lambda)$ was obtained.

The stress p in the specimen, measured in bars (megadynes per square centimetre), was calculated from the applied weights and the dimensions of the apparatus, on the assumption that the thrust is uniformly distributed at

a distance from the loaded ends of the specimen. This will still give the correct mechanical stress at the centre of the specimen, even if there is a buckling moment.

In order to obtain the observed retardation we have to add to p a correction Δp , which represents the so-called "residual stress," although in actual fact there need be no internal stress corresponding to it.* It is assumed that the axes of polarisation of the specimen, when unloaded, are longitudinal and transverse; this was found to be very approximately the case.

6. A preliminary set of observations, in which r was plotted to p , indicated approximately a linear relation between r and p for the observations of each separate order n .

This may be written

$$r = C_0 p d + B_n, \quad (2)$$

where

$$r = n\lambda. \quad (3)$$

If we now assume that the law of proportionality of retardation to stress, for light of a given wave-length, a law hitherto verified for glasses within the limits of observation, holds also for silica, we obtain the further equation

$$r = C(p + \Delta p)d, \quad (4)$$

where C is the usual stress-optical coefficient for light of wave-length λ .

Eliminating r and p between (2), (3) and (4), we obtain the relation between C and λ

$$C = C_0 / \left(1 - \frac{\{B_n - C_0 \Delta p \cdot d\}}{n\lambda} \right). \quad (5)$$

Since by hypothesis C should be independent of the stress, and therefore of the order n of the band, $(B_n - C_0 \Delta p \cdot d)/n$ should be a constant, or

$$B_n = n\lambda_0 + C_0 \Delta p \cdot d, \quad (6)$$

so that

$$C = C_0 / (1 - \lambda_0 / \lambda). \quad (7)$$

The law (7) is identical with that found by Filon† to give the general characteristics of photo-elastic dispersion for a number of glasses. It is thus seen to apply also, fairly closely, to vitreous silica.

From the observed values of B_1 , B_2 , we have :

$$B_1 = \lambda_0 + C_0 \cdot \Delta p \cdot d, \quad (8)$$

$$B_2 = 2\lambda_0 + C_0 \cdot \Delta p \cdot d, \quad (9)$$

* See Filon and Harris, 'Proc. Roy. Soc.,' A, vol. 103, pp. 561-571 (1923).

† 'Phil. Trans.,' A, vol. 207, pp. 280-287 (1907).

two equations from which λ_0 and Δp can be found. The preliminary observations gave the rough values :—

$$C_0 = 3.331 \text{ brewsters (1 brewster} = 10^{-13} \text{ cm.}^2/\text{dyne)}$$

$$\lambda_0 = 540 \text{ \AA.}$$

$$\Delta p = -6.06 \text{ bars.}$$

Comparison between the theoretical straight line and the observations, however, appeared to indicate systematic residuals from the formula (7) in the neighbourhood of the wave-lengths λ 5000 and λ 6000. If we now denote by C' the stress-optical coefficient calculated from formula (7), C denoting the observed ratio of retardation to stress per unit thickness, $C - C'$ showed a change from $+$ to $-$ as we passed from λ 4900 to λ 5100. Only two observations were involved, but it so happens that a precisely similar variation was detected by Filon* in an investigation of the photo-elastic dispersion of a number of glasses. This had been ascribed at the time to a constituent such as PbO or B_2O_3 . Its occurrence in pure silica, if confirmed, would lead to a new interpretation of the older results.

7. A fresh set of observations was then taken, with loads at closer intervals, and a formula of the type

$$r = C_0(p + \Delta p)d + n\lambda_0 \quad (10)$$

fitted to the observations by least squares for the unknowns C_0d , $C_0\Delta p \cdot d$, λ_0 , giving the following values :

$$\left. \begin{aligned} C_0 &= 3.3775 \text{ brewsters} \\ \lambda_0 &= 431.5 \text{ \AA.} \\ \Delta p &= -5.43 \text{ bars} \end{aligned} \right\} \quad (11)$$

As the stress in the specimen varied from 134.18 to 424.00 bars, the agreement between this value of Δp and the one previously found by rough calculations for a different experiment was very satisfactory. The value of Δp given by (11) was therefore adopted and applied as a correction to all the calculated mechanical stresses p .

The values of C were then computed from the observed retardations r and the corrected stresses $p + \Delta p$, by the formula

$$C = r/(p + \Delta p)d, \quad (12)$$

* *Loc. cit.*, pp. 293-301 (1907).

and the values of C' were calculated from the formula (7), using the values of C_0 , λ_0 given by (11).

The results are given in Table I below, the differences $C - C'$, i.e., C observed — C calculated from the standard formula, being given in the fourth column in millibrewsters.

The values of $C - C'$, given by Table I, are plotted to λ in fig. 1. The agreement between the values given by different orders is remarkable; in a number of cases the values yielded by the first and second orders give almost coincident points on the diagram.

Table I.—Observations of Silica (Specimen A), 1924.

Order I.				Order II.			
λ .	C .	C' .	$C - C'$.	λ .	C .	C' .	$C - C'$.
4316	3.717	3.753	—36	4245	3.768	3.760	+ 8
4468	3.741	3.739	+ 2	4353	3.754	3.749	+ 5
4580	3.731	3.729	+ 2	4470	3.747	3.738	+ 9
4710	3.736	3.718	+18	4578	3.734	3.729	+ 5
4825	3.730	3.709	+21	4698	3.732	3.719	+13
4905	3.697	3.703	— 6	4812	3.724	3.710	+14
5003	3.679	3.696	—17	4918	3.711	3.702	+ 9
5115	3.672	3.689	—17	5012	3.690	3.696	— 6
5233	3.670	3.681	—11	5100	3.665	3.690	—25
5363	3.676	3.673	+ 3	5228	3.670	3.681	—11
5465	3.662	3.667	— 5	5340	3.664	3.674	—10
5578	3.657	3.661	— 4	5440	3.649	3.669	—20
5685	3.648	3.655	— 7	5565	3.652	3.661	— 9
5788	3.637	3.650	—13	5678	3.647	3.655	— 8
5910	3.638	3.644	— 6	5790	3.642	3.650	— 8
6035	3.641	3.638	+ 3	5910	3.641	3.644	— 3
6158	3.642	3.632	+10	6035	3.644	3.638	+ 6
6265	3.634	3.627	+ 7	6140	3.635	3.633	+ 2
6400	3.643	3.622	+21	6258	3.634	3.628	+ 6
6510	3.637	3.617	+20	6400	3.646	3.622	+24
6628	3.636	3.613	+23	6505	3.637	3.618	+19
6700	3.610	3.610	0	6583	3.614	3.614	0
6785	3.591	3.607	—16	6680	3.602	3.611	— 9
				6780	3.592	3.607	—15

Order III.			
λ .	C .	C' .	$C - C'$.
4378	3.741	3.747	— 6
4460	3.741	3.739	+ 2
4586	3.735	3.733	+ 2
4610	3.729	3.726	+ 3
4685	3.723	3.720	+ 3

The black curve in fig. 1 is drawn freehand through the observations and is intended as an aid to exhibit their most marked characteristics. Of these the

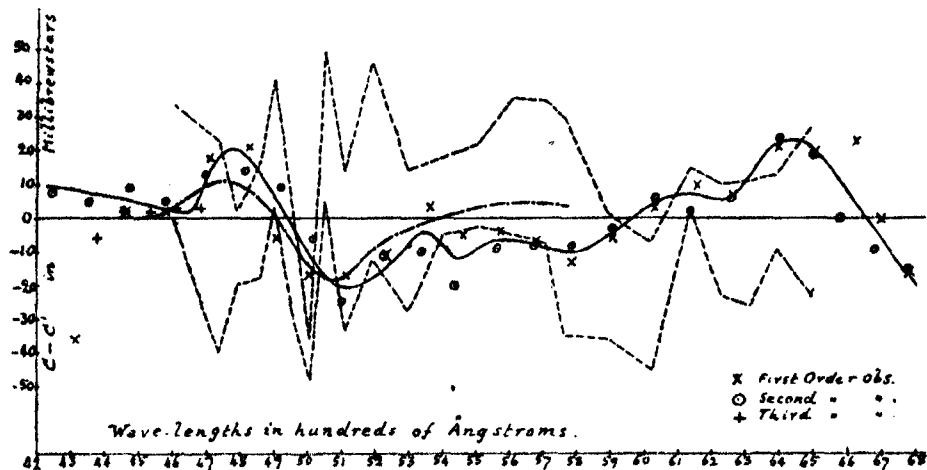


FIG. 1.

chief is the rise of the curve about $\lambda 4800$ and its gradual fall to a minimum about $\lambda 5100$, followed by a subsequent rise. For purposes of comparison fig. 10 of Filon's 1907 paper has been recalculated, so as to exhibit $C - C'$ in millibrewsters and is here shown by the curve of dots and dashes in fig. 1. This curve, which refers to a glass (3453) containing 20.8 per cent. of K_2O , 5.7 per cent. of B_2O_3 and 5.4 per cent. of MgO , but only 68.1 per cent. of silica, is seen to exhibit precisely the same type of curve of deviations as the one found here for silica. A very similar oscillation of approximately the same extent was found also in another glass (3296) with a silica content of 67.5 per cent. It is noteworthy that the two glasses which then showed this effect to a marked degree were precisely those which contained a large percentage of silica, and none of those with a smaller silica content (35.4, 32.5, 31.6) per cent. showed it appreciably. It is a curious coincidence that the amplitudes of the oscillation in the glasses 3453 and 3296 on the one hand, and in pure silica on the other, are roughly 28 and 40 millibrewsters respectively, or approximately as the silica contents in the two cases. In any case it now appears very probable that silica is responsible for this particular irregularity.

The present observations, however, indicate other, but less marked, irregularities. There is an indication of another wave about $\lambda 5400$ and a marked gradual rise from $\lambda 5800$ to $\lambda 6100$, followed by a slight fall, and a further rise to a maximum about $\lambda 6450$, with a sharp subsequent fall. The last rise and

fall are also indicated roughly in Filon's 1907 paper and are probably significant. The maximum at about λ 6100, although not very clearly marked here, should be noted, in reference to subsequent results.

8. In view of the importance of the above observations from the standpoint of the theory of photo-elasticity, it was considered essential to confirm them by an independent method, which should be free from certain defects inherent in the spectrometer method as used by us previously.

The defects which we had in mind at the time were two-fold. In the first place, any error in determining the centre of a band affected, not merely the calculated retardation, but the wave-length of the observation. Thus, in the plotted curves, not only the ordinates, but the abscissæ were liable to uncertainty. In the case of rapid local variations, this might easily distort the curve appreciably.

In the second place, the load had necessarily to be varied from observation to observation. If the variation of the load (*a*) did not affect its distribution in the specimen and (*b*) caused no lateral displacement of the specimen; and further, if (*c*) the law of proportionality of retardation to stress held good rigorously, then this progressive alteration of load could introduce no error. But previous experience had shown that changes of load inevitably introduced (*a*) and (*b*); and although the method described in § 3 allowed these effects to be corrected and minimised, they could not be altogether got rid of.

Even more fundamental was the uncertainty as to (*c*). Although, so far, no deviation from this law of proportionality had been recognised for glass, the accuracy of the observations establishing it fell far short of the accuracy here aimed at in the determination of *C*. At the time, however, we attached no great importance to this source of error. But the later results of S. R. Savur, on the photo-elastic dispersion of overstrained celluloid, showed clearly that, in this material, the law of variation of *C* with the wave-length was fundamentally affected by overstrain; this suggested that there was at least a possibility that, in glasses, *C* might be a function, not only of λ , but of the stress; in which case the relation between retardation and stress, for a given λ , could no longer be one of simple proportionality.

It was therefore necessary to devise a method of measuring *C* throughout the spectrum, at definite wave-lengths, and with the specimen under constant load, undisturbed throughout the series of observations.

A great deal of preliminary work was necessary before such a method could be devised and made to work with the necessary accuracy. Pressure of other

work interrupted the observations and it was not until 1929 that it was possible to obtain reliable results.

As it turned out the results obtained by the new method revealed an unsuspected source of error, due to the character of the variations under investigation, which seriously vitiated the accuracy of the earlier observations.

9. In the new method a plate of quartz of adjustable thickness was introduced in the path of the light between the analyser and the specimen. The plate was made like a Babinet compensator and consisted of two similar thin wedges of quartz, whose relative motion was controlled by a specially constructed micrometer screw. The axes of polarisation of the plate were parallel and perpendicular to the line of stress in the specimen.

Apart from this the apparatus remained unaltered in essentials. The spectroscope was of the Littrow type, giving a high dispersion, and was provided with a reading microscope furnished with graticules and a micrometer.

Initially the specimen was under the small compression due to the weight of the lever arm and hangers only.

The retardation of the plate alone (about 43λ for sodium light) produces in the visible spectrum about 20 fairly sharp bands.

Using the iron comparison spectrum, the zero of the reading microscope was set upon a standard iron line. On removing the comparison spectrum, the banded spectrum, due to the plate and slightly stressed specimen, was visible. The quartz plate micrometer was then adjusted until the band of order n_0 was brought to the zero of the reading microscope, x_0 being the reading of the quartz plate micrometer when this occurs. An additional load W was now applied to the lever of the straining apparatus and the band of order $n_0 + m$ was brought to the zero of the reading microscope, the observed reading of the quartz plate micrometer being then x . The bands can be identified by continuous observation, or from a preliminary approximate experiment, so that m is a known integer in every case; it is unnecessary to determine the absolute order n_0 .

This procedure was repeated for 23 standard iron lines between λ 4500 and λ 6500, the extreme red and extreme violet being omitted owing to the reduced illumination with the high dispersion spectroscope.

The whole of the observations at each load were taken without changing the load, or altering the condition of the specimen. This involved re-setting the zero of the reading microscope on all the standards selected for each separate load, but it entirely eliminated any effects due to possible displacement of the specimen on loading and unloading, as between one wave-length and another.

If now r_0 is the initial retardation of the specimen ; r the additional retardation due to a load W ; ρ_0 the retardation produced by the quartz when the micrometer reading is x_0 ; ρ the retardation produced by the quartz when the micrometer reading is x ; then we have

$$n_0\lambda = r_0 + \rho_0,$$

$$(n_0 + m)\lambda = r_0 + r + \rho.$$

Hence

$$m\lambda = r + (\rho - \rho_0). \quad (13)$$

Now let s be the difference of the micrometer readings required to produce an additional retardation of a whole wave-length in the light of length λ .

Then $(\rho - \rho_0)/\lambda = (x - x_0)/s$, so that equation (13) can be written

$$r = \lambda[m - (x - x_0)/s], \quad (14)$$

which determines r , the retardation due to the addition of the weight W , directly.

Thus r is found for each of the 23 standard wave-lengths, and, since r is equal to the difference of the refractive indices in the silica, multiplied by the thickness traversed, this difference of refractive indices, caused by the addition of W , is measured independently of any assumption as to the stress-optical relation.

In practice, however, it is convenient to express the result as a stress-optical coefficient, by dividing the difference of refracting indices in question by the stress corresponding to the load W . Even if this calculated stress is not exactly equal to the actual pressure at the point observed, the effect is merely to apply to the results a constant factor, nearly equal to unity, which leaves the law of dispersion unaffected.

10. To use formula (14) it is necessary to obtain s for the particular wave-length of the observation. This is done immediately by moving the quartz plate micrometer until the next band comes on the zero of the reading microscope and noting the difference of the micrometer readings.

In view of the importance of determining s accurately, and as a check on any possible errors of the micrometer screw, the following procedure was adopted.

A fresh set of readings of s was taken simultaneously with every set of observations ; the products

$$(\mu_2 - \mu_1)s/\lambda$$

were formed, where $\mu_2 - \mu_1$ is the difference of the refractive indices of quartz for wave-length λ , obtained from the table of values of $\mu_2 - \mu_1$ previously

determined by F. C. Harris.* These products should all have the same value; owing to inevitable errors of observation they were found to differ slightly. The arithmetic mean of all these products was found and this was taken as the correct value of the product. s was then calculated by multiplying this mean value by $\lambda/(\mu_2 - \mu_1)$. In this way a value of s was obtained which was practically independent of the individual observation.

At the same time the various readings for s for different sets all corresponded to different readings of the micrometer screw and their agreement supplied evidence of the freedom of the latter from periodic or other errors.

Two typical sets of such readings, for the wave-lengths $\lambda 5763.013$ and $\lambda 4957.606$, are given below.

$\lambda 5763.013.$		$\lambda 4957.606.$	
Reading for s .	Div. from mean.	Reading for s .	Div. from mean.
r		r	
19.44	+0.12	16.25	-0.09
19.30	-0.02	16.32	-0.02
19.28	-0.04	16.34	0.00
19.34	+0.02	16.42	+0.08
19.31	-0.01	16.26	-0.08
19.35	+0.03	16.34	0.00
19.25	-0.07	16.46	+0.12
19.37	+0.05	16.36	+0.02
19.27	-0.05		
19.32	0.045	16.34	0.054
mean s .	mean error.	mean s .	mean error.

It may therefore be taken that the mean error of a difference of settings is about 0.05 of a revolution of the screw. This will also apply to the differences $x - x_0$. For the case where the retardation is as high as 2λ , this amounts to an error of 5 in about 4000, or a little over 1/10 per cent. Near the ends of the range, however, where the illumination is poor, the error may be somewhat larger than this. For values of W corresponding to smaller retardations, the error is proportionately greater; it will, on the other hand, be less for higher values of W . Thus more weight must be attached to the observations with the higher values of W , the weight (in the sense of the theory of probability) being in fact proportional to W .

11. For this set of observations specimen B was used. This (see § 2) was a good deal larger than the earlier ones and it was possible to attain a retardation

* 'Phil. Mag.' vol. 7, pp. 80-85 (1929).

of 2λ without risk of breakage, or exceeding the probable limit of elasticity. The strength of the lever arm, however, limited the load W .

The results for six different loads $W = 10, 20, 25, 30, 35$ and 40 kilogrammes weight, corresponding to calculated additions of pressure in the specimen of $19.437, 38.874, 48.593, 58.311, 68.030$ and 77.748 bars respectively, are given in Tables II (a), (b), (c), (d), (e) and (f).

The left-hand column, common to all the tables, gives the wave-length of the observation; the first column of each table gives the stress-optical coefficient C , calculated from the observed retardation; the second column gives the quantity C' calculated from the formula $C' = C_0/(1 - \lambda_0/\lambda)$, C_0 and λ_0 having been determined by a least square fit of the given set of observations; and the third column gives $C - C'$, this last in millibrewsters, C and C' being given in brewsters.

Table II.

λ	(a)			(b)			(c)		
	$W=10$ kgm. Stress = 19.437 bars. $C_0=2.840$ brewsters. $\lambda_0=1158.5$ Å.			$W=20$ kgm. Stress = 38.874 bars. $C_0=3.065$ brewsters. $\lambda_0=825.2$ Å.			$W=25$ kgm. Stress = 48.593 bars. $C_0=3.390$ brewsters. $\lambda_0=427.4$ Å.		
	C	C'	$C-C'$	C	C'	$C-C'$	C	C'	$C-C'$
6494.993	3.439	3.457	-18	3.517	3.511	+ 6	3.606	3.629	-23
6393.612	3.505	3.469	+36	3.511	3.520	- 9	3.624	3.633	- 9
6318.028	3.497	3.478	+19	3.500	3.526	-26	3.646	3.636	+10
6230.734	3.508	3.489	+19	3.543	3.533	+10	3.638	3.640	- 2
6136.624	3.554	3.501	+53	3.547	3.541	+ 6	3.656	3.644	+12
6027.059	3.500	3.516	-16	3.522	3.552	-30	3.642	3.649	- 7
5895.932	3.531	3.535	- 4	3.566	3.564	+ 2	3.622	3.655	-33
5763.013	3.518	3.555	-37	3.608	3.578	+30	3.664	3.662	+ 2
5709.396	3.543	3.563	-20	3.610	3.583	+27	3.700	3.665	+35
5615.661	3.553	3.579	-26	3.629	3.593	+36	3.692	3.670	+22
5506.784	3.559	3.597	-38	3.628	3.606	+22	3.681	3.676	+ 5
5397.134	3.645	3.617	+28	3.614	3.619	- 5	3.687	3.682	+ 5
5302.315	3.587	3.634	-47	3.602	3.630	-28	3.702	3.688	+14
5192.363	3.626	3.656	-30	3.633	3.645	-12	3.740	3.694	+46
5110.415	3.596	3.673	-77	3.622	3.656	-34	3.714	3.700	+14
5049.827	3.710	3.686	+24	3.669	3.664	+ 5	3.730	3.704	+26
5006.130	3.660	3.696	-36	3.621	3.670	-39	3.665	3.707	-42
4957.606	3.703	3.707	- 4	3.679	3.677	+ 2	3.680	3.710	-30
4903.335	3.797	3.719	+78	3.689	3.686	+ 3	3.728	3.714	+14
4859.657	3.729	3.729	0	3.702	3.692	+10	3.699	3.717	-18
4789.657	3.777	3.747	+30	3.705	3.703	+ 2	3.702	3.722	-20
4736.786	3.745	3.760	-15	3.735	3.712	+23	3.687	3.727	-40
4602.946	3.897	3.786	+101	3.735	3.735	0	3.755	3.737	+18

Table II—(continued).

	(d)			(e)			(f)		
	W=30 kgm. Stress=58·311 bars. C ₀ =3·340 brewsters. λ ₀ =474·5 Å.			W=35 kgm. Stress=68·030 bars. C ₀ =3·265 brewsters. λ ₀ =521·1 Å.			W=40 kgm. Stress=77·748 bars. C ₀ =3·122 brewsters. λ ₀ =780·7 Å.		
λ.	C.	C'.	C-C'.	C.	C'.	C-C'.	C.	C'.	C-C'.
6494·993	3·630	3·603	+27	3·572	3·550	+22	3·548	3·549	- 1
6393·612	3·620	3·607	+13	3·568	3·555	+13	3·554	3·557	- 3
6318·028	3·622	3·611	+11	3·547	3·559	-12	3·555	3·562	- 7
6230·734	3·604	3·615	-11	3·540	3·563	-23	3·576	3·570	+ 6
6136·624	3·634	3·619	+15	3·572	3·568	+ 4	3·585	3·577	+ 8
6027·059	3·580	3·625	-45	3·554	3·574	-20	3·571	3·587	-16
5895·932	3·594	3·632	-36	3·581	3·582	- 1	3·585	3·599	-14
5763·013	3·604	3·639	-35	3·606	3·590	+16	3·625	3·611	+14
5709·396	3·669	3·642	+27	3·586	3·593	- 7	3·630	3·617	+13
5615·661	3·649	3·648	+ 1	3·594	3·599	- 5	3·638	3·626	+12
5506·784	3·675	3·654	+21	3·605	3·607	- 2	3·654	3·638	+16
5397·134	3·662	3·661	+ 1	3·611	3·614	- 3	3·668	3·650	+18
5302·315	3·661	3·668	- 7	3·628	3·621	+ 7	3·646	3·661	-15
5192·363	3·683	3·675	+ 8	3·649	3·630	+19	3·672	3·675	- 3
5110·415	3·682	3·681	+ 1	3·639	3·636	+ 3	3·659	3·685	-26
5049·827	3·735	3·686	+49	3·663	3·641	+22	3·705	3·693	+12
5006·130	3·642	3·689	-47	3·607	3·645	-38	3·663	3·699	-36
4957·606	3·678	3·693	-15	3·636	3·649	-13	3·678	3·706	-28
4903·325	3·738	3·697	+41	3·692	3·664	+28	3·740	3·713	+27
4859·657	3·706	3·701	+ 5	3·645	3·657	-12	3·737	3·720	+17
4789·657	3·693	3·707	-14	3·655	3·664	- 9	3·718	3·730	-12
4736·786	3·683	3·711	-28	3·661	3·669	- 8	3·729	3·738	- 9
4602·946	3·757	3·723	+34	3·690	3·682	+ 8	3·789	3·760	+29

12. The results of Table II show a regular alteration of the constants C_0 , λ_0 with the load.

Although no very great importance need be attached to the particular form of the relation (7), which is purely empirical, nevertheless these constants are useful as giving a measure of the general trend of the photo-elastic dispersion. The constant C_0 appears to increase to a maximum for $W = 25$ and then to decrease, and simultaneously there is a fall of λ_0 to a minimum and a subsequent rise.

The variation of C_0 might be explained away on the supposition that, as the load is altered, some displacement of the specimen or buckling effect causes the stress at the point observed to depart from the calculated mean pressure, thereby altering the scale-value for C . But such an explanation clearly fails to account for the variation of λ_0 , and, in view of the fact that the two variations are obviously connected, it seems highly probable that both are significant.

If this is correct it indicates that, even for such comparatively moderate pressures, the retardation, in silica, is not strictly proportional to the applied load, a result of very great importance, as it contradicts one of the fundamental assumptions of photo-elastic theory, an assumption hitherto accepted without question, at any rate in the case of glass, though deviations from the law are known to exist in the case of nitro-cellulose and other organic compounds.

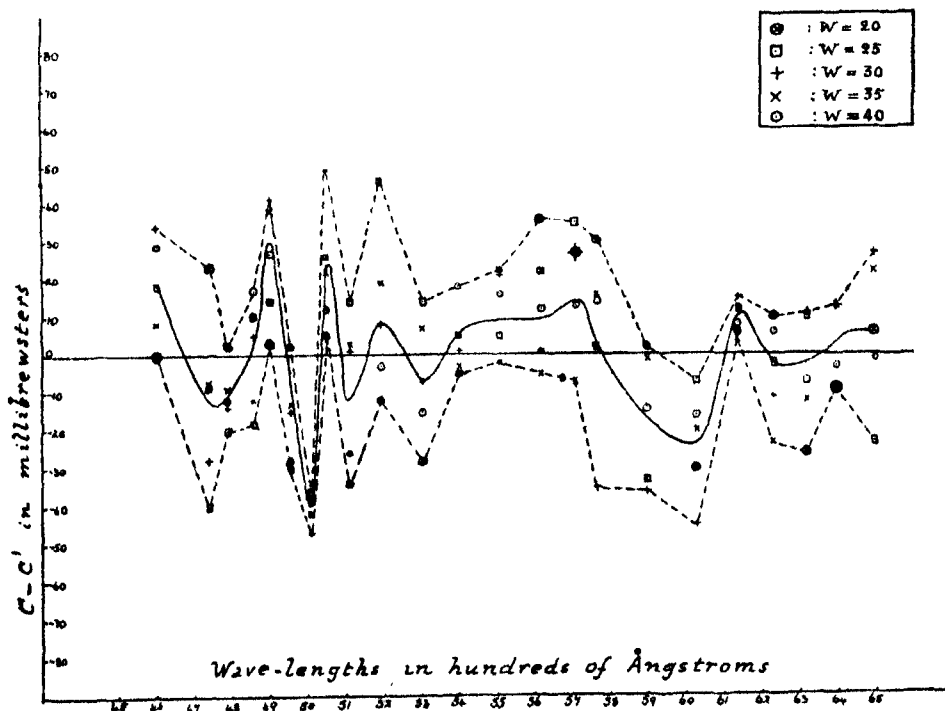


FIG. 2.

13. Coming now to the local deviations ($C - C'$ of Table II), these are exhibited in the diagram of fig. 2, with the exception of the observations for $W = 10$. As previously explained, the weight attaching to these last individual observations is only slight, and this is well shown by the large and irregular residuals, although some of the more striking characteristics, *e.g.*, the dips at $\lambda 5006$ and $\lambda 6027$ and the peak at $\lambda 4903$, are clearly shown even in this set.

The full curve in fig. 2 is drawn through the weighted mean of the values of $C - C'$, and in this weighted mean the observations for $W = 10$ have been included.

The lines of dashes in fig. 2 are drawn so as to join the outermost observations of successive wave-lengths so that the area between them includes all observa-

tions for $W > 10$. It will be seen that these upper and lower limiting lines correspond closely in their characteristics; and in those cases where a peak of the lower line, *e.g.*, at $\lambda 5050$, rises well over an adjacent dip of the upper line, *e.g.*, at $\lambda 5006$, the existence of a real oscillation in the curve cannot be doubted. Indeed it seems probable that most, if not all, of the oscillations shown by the full curve are significant.

In interpreting the diagram it must be borne in mind that the formula for C' adopted for comparison has no theoretical justification. Many other formulæ giving a smooth variation might equally well have been fitted; all would have brought out sharp local variations, but some might have better reconciled divergences extending over a wide range between observations of different sets. Conclusions must therefore be limited to undoubted oscillations over a short range of λ .

Further the "scatter" of the values of $C - C'$ is largely due to the scale on which the ordinates have been plotted, for clearness. It must be remembered that the probable error of an individual value of C may well be as great as 10 millibrewsters in many cases, and is certainly never less than 5 millibrewsters.

Nevertheless, when all the above considerations have been allowed for, there remain the following characteristics which appear to be certainly significant.

- (1) A rise of about 40 millibrewsters from $\lambda 4790$ to a peak at $\lambda 4903$.
- (2) A sharp fall of about 70 millibrewsters from $\lambda 4903$ to a sharply characterised dip at $\lambda 5006$.
- (3) An equally sharp succeeding rise of about 60 millibrewsters to a peak at $\lambda 5050$, followed by a fall of about 35 millibrewsters to a dip at $\lambda 5110$.
- (4) A general (but more gradual) fall from $\lambda 5700$ to a dip at $\lambda 6027$.
- (5) A sharp rise of about 35 millibrewsters from $\lambda 6027$ to a peak at $\lambda 6137$, followed by a less clearly defined fall.

14. If we now compare these results with those of the 1924 observations shown by fig. 1, in which the interrupted lines of fig. 2 have been reproduced, it appears that, although the fall from $\lambda 4900$ to $\lambda 5000$ and the maximum near $\lambda 6150$ are shown by the earlier curve, this curve seems in some way to smooth out several of the sharp oscillations revealed by the later observations. This might be due to the fact that the 1924 observations happen to have missed out some of the actual peaks and dips; if we bear in mind that in fig. 1 the abscissæ, as well as the ordinates, are liable to error, it is seen that a slight readjustment will bring the observations between $\lambda 4850$ and $\lambda 5100$ into fair agreement.

The curve of dots and dashes in fig. 1, however, which is based on observations taken at closer intervals, cannot be explained in this manner, and, if the discrepancy between figs. 1 and 2 were to be accounted for in this way, the correspondence between the silica and the glass (and, after all, it is *a priori* probable that the silica contained in the latter must produce its effect) would disappear.

The possibility that specimens A and B may not have been identical as regards their photo-elastic properties cannot be dismissed without examination. Unfortunately the observations of specimen A taken by the second method are few in number, this specimen having eventually been discarded in favour of the larger and more perfect specimen B. Also these observations belong to an early stage, before the method had been improved so as to give all the accuracy of which it is capable and their probable error is therefore much higher than that of the observations of Table II.

Nevertheless, one of the most reliable sets of these observations of specimen A was worked out and the corresponding values of $C - C'$ are shown by the black dots of fig. 3, which also shows the lines of dashes giving the limits between which lie the observations of specimen B.

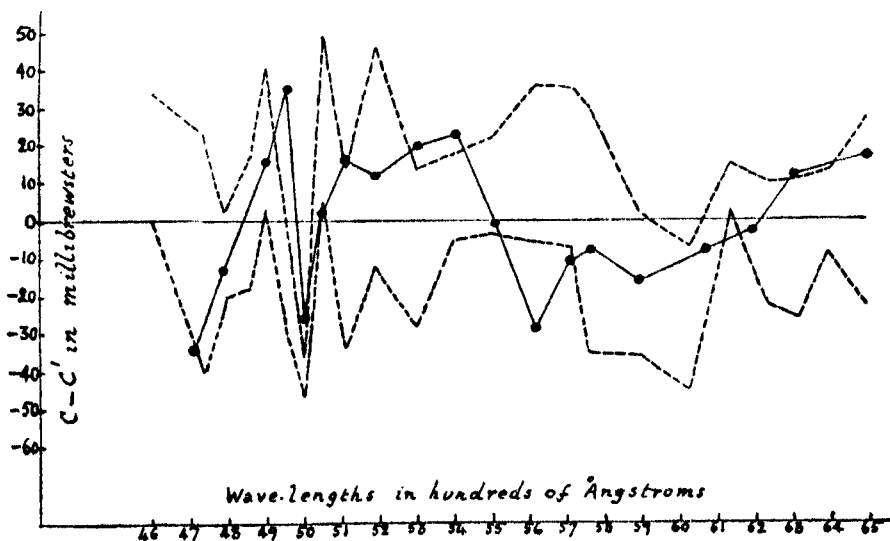


FIG. 3.

Such as they are, these observations of specimen A lie either close to, or within, the limits marked by the lines of dashes. The only important deviations occur at $\lambda 4958$ and $\lambda 5616$ and these are, in all probability, accidental. The

dip at $\lambda 5000$, with the immediate rise on either side, is confirmed, and so is the sharp rise from $\lambda 4750$ to $\lambda 4900$. The dip and peak at $\lambda 6025$ and $\lambda 6135$ respectively are not shown, but then observations at these points happen to be lacking. The peak at $\lambda 5192$ and the dips at $\lambda 5110$, 5302 are missing; these, however, being of minor extent, are liable to be obliterated by the errors of observation in the present case.

The important thing here is the character of the variation over the range $\lambda 4750$ to $\lambda 5100$, and it is clear that the observations of fig. 3 harmonise better, in this respect, with the observations of specimen B than with the earlier ones of specimen A.

15. It appears therefore probable that the smoothing out of the oscillations, in the original observations, is in some way connected with the character of these observations. A re-examination of the method explained in § 5, in the light of the results of Table II, strongly confirms this.

The stress-optical coefficient was obtained from equation (12), which may be written

$$C/\lambda = n/(p + \Delta p)d, \quad (15)$$

the roots in λ of this equation giving the centres of the dark bands in the spectrum.

So long as there are no turning points in the function C/λ , (15) will have a well-defined single root for every value of the right-hand side within the range considered.

This is no longer the case if C/λ has turning points. Consider the full curve of fig. 4, which has been accurately plotted from the weighted means of C obtained from Table II. It will be seen that, owing to the oscillations already mentioned, there are two turning points of C/λ at about $\lambda 5000$ and $\lambda 5050$. Now if we draw a horizontal line PQ of ordinate $n/(p + \Delta p)d$, its intersections with the curve give the centres of the black bands. As p is increased PQ moves downwards, there being only one intersection until PQ touches the curve at the upper turning point ($\lambda 5050$). From this time on there are *three* intersections, so that, in strictness, what is observed is a *triple* band. This state of things goes on until PQ touches the curve at the lower turning point ($\lambda 5000$), after which the band is single.

In practice, however, the eye fails to resolve the triple band, and integrates it into a single band, to which it ascribes a fictitious centre. What happens is that the region of fairly uniform darkness extends within limits given by $(n \pm \nu)\lambda$, where ν is a fraction which may be estimated at between $1/20$ and

1/40. The values of λ which fall inside this region are given by the intersections of the full curve of fig. 4, not with a single line PQ, but with a horizontal

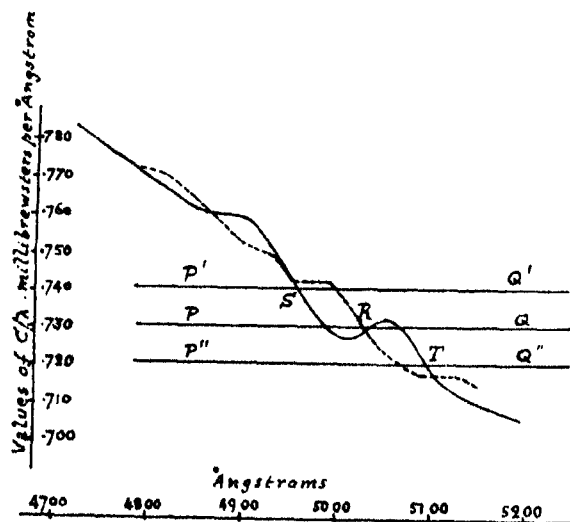


FIG. 4.

strip bounded by two parallel horizontal lines $P'Q'$, $P''Q''$ of ordinates $(n \pm \nu)/(p + \Delta p)d$. When this strip penetrates the peak at $\lambda 5050$, a second band begins to appear to the right of the first one, but so soon as $P''Q''$ has fallen below the level of the left-hand turning point, all that would be visible would be a broadening of the band. When $P'Q'$ falls below the level of the right-hand turning point this broad band again splits up, the left (or violetward) component becoming progressively narrower and fainter.

Owing to the small range of the oscillation in question (50 Å.) and the fact that these bands have no sharp edges, the gradation from darkness to light being by no means steep, the actual observation of this splitting up would be very difficult, and very easily entirely missed, unless the effect was deliberately looked for, which was not the case.*

Some sort of estimate of the error made can be arrived at by considering the point R on PQ exactly half-way between the extreme intersections S, T of the strip with the curve. R would correspond to the centre of a band if placed exactly half-way between the limits of "darkness" as defined above, neglecting any intermediate restoration of light.

* *Note added November 25, 1930.*—By a series of multiple reflections, thus increasing the path and magnifying the retardation, without the use of quartz wedges, the splitting up in question has since been observed.

The locus of R is shown by the dotted line in fig. 4. There are, of course, two discontinuities, shown by straight horizontal portions, corresponding to the stages where the edges of the strip cross the curve of C/λ at the turning points.

If the points R corresponded to the estimated centres of the bands, the values of C obtained by the older method would be derived from this locus, which is obviously very different from the original, and, in particular, possesses no turning points. It is in fact obtained from the original by a classical process of "smoothing," replacing a pair of points on the curve, at constant vertical interval, by the midpoint of their chord.

It will be noticed also that the locus of R deviates from the original, not merely near a pair of turning points, but whenever there is any rapid change of direction of the curve of C/λ , *e.g.*, near λ 4850 and λ 4900.

It would be unprofitable, however, to pursue this line of argument further, for the precise manner in which the eye centres such a compound or unsymmetrical band is really quite uncertain. Enough has been said to show that the result will inevitably be to smooth out rapid oscillations, and we need look no further for the cause of the discrepancy between the 1924 and 1930 observations.

It is clear that the later method, which is unaffected by this source of error, owing to the steep gradient introduced by the quartz, is alone reliable when rapid oscillations are in question, and the 1924 results would not have been included here had it not been that they connect up with the 1907 observations of the glasses 3453 and 3296 and provide the explanation of the irregularities observed in these glasses.

16. The physical interpretation of the anomalous dispersion shown by fig. 2 is a matter of some difficulty. Filon, in the 1907 paper, quoted previously, suggested that there existed a kind of latent absorption band, due to a free period of the constituents of the glass, which absorption band was, so to speak, brought out by the stress. He was, however, unable to identify this free period, owing partly to the difficulty of localising it from his curve, partly to the multiplicity of constituents in his glasses.

In the present case the limits of the oscillations are much narrower; the highly localised character of these oscillations suggests inevitably that some free periods are active; but other difficulties of identification now occur. If we follow the analogy of the ordinary curves of anomalous dispersion, a single free period causes a single dip and peak, the wave-length of the free period coming midway between the two. If we apply this principle to fig. 2,

the critical wave-lengths should be about 4840, 5025, 5150, 6090 and possibly 6350, if we associate with each dip the peak immediately on its redward side, which is the usual form of anomalous dispersion.

On the other hand, there is here no reason why the sign of the variation should not be reversed, in which case the critical wave-lengths should be about 4680, 4950, 5090, 5250 and possibly 6200.

But when we have to deal with several free periods fairly close together, the appearances may depart considerably from the simple peak and dip form.

This is illustrated by fig. 5, which combines two "peak and dip" curves of the form

$$y_1 = A_1 \alpha_1 (\lambda - \lambda_1) / \{(\lambda - \lambda_1)^2 + \alpha_1^2\}$$

$$y_2 = A_2 \alpha_2 (\lambda - \lambda_2) / \{(\lambda - \lambda_2)^2 + \alpha_2^2\},$$

the form in question being obtained from any standard anomalous dispersion formula, treating λ as approximately constant except when it enters into the difference $\lambda - \lambda_n$. This gives a sufficient approximation for our purpose.

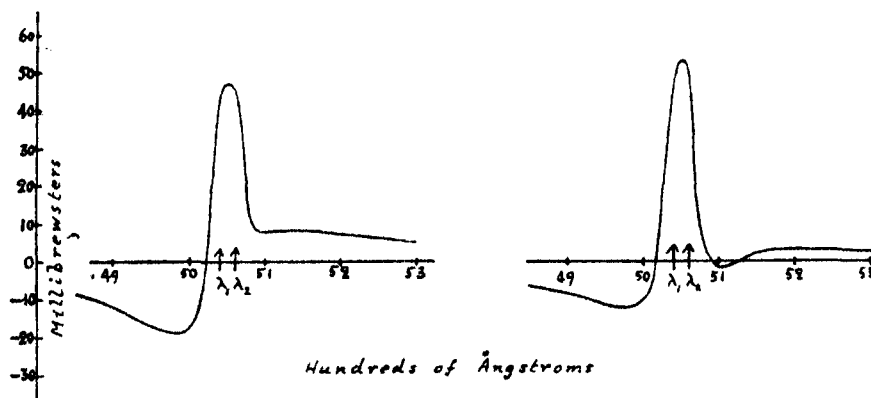


FIG. 5A.

FIG. 5B.

Fig. 5A is calculated from the assumed values $\lambda_1 = 5040$, $\lambda_2 = 5060$, $\alpha_1 = 40$ Å., $\alpha_2 = 30$ Å., $A_1 = 100$ millibrewsters, $A_2 = -80$ millibrewsters; fig. 5B is drawn for the same values, except that A_2 has been taken equal to -100 millibrewsters, that is, to $-A_1$. It will be seen from these figures that it is possible, by combining two near free periods with coefficients of opposite sign, to produce a sharp peak with dips on either side. Thus the dips at 4980 in figs. 5A and 5B are actually produced by the pair of wave-lengths 5040, 5060. We may therefore have these dips (or peaks, by reversing the sign) occurring at points some distance away from the free periods responsible;

nor do these latter necessarily fall, as in the case of a single free period, between a dip and a peak.

Now the general characteristics of the full curve of fig. 2 suggest that we may here have to deal with one or more oscillations of this nature.

The question which at once arises is whether any of the known lines of silicon or oxygen is connected with the effect. Since silica seems alone active in this respect among the various oxides which constitute glasses, it would seem *prima facie* that we need not consider oxygen, at any rate so far as its atomic vibrations are concerned.

If we now turn to the silicon spectrum, we find (see A. Fowler, 'Phil. Trans.,' A, vol. 225, pp. 1-48 (1924)) that the most intense lines of silicon in the region under consideration are :—

- A. Two strong lines at λ 5041 and 5056.
- B. Two strong lines at λ 6347 and 6371.
- C. Two fairly strong lines at λ 4568 and 4553.
- D. Three (weaker) lines at λ 5949, 5958 and 5979.
- E. Two moderately strong lines at λ 5708 and 5740.
- F. One weak line at λ 4717.

The pair C is practically outside the range of observation, although, in combination with F, it may very well have influenced the curve between 4600 and 5000. Groups B and D may be jointly responsible for the peak at 6135 and the oscillations in that region, but it is practically impossible to disentangle the effects. The pair E may be associated with the beginning of the marked dip from 5700 onwards. The pair A is the one which might be most hopefully traced, being more or less isolated in this region. It may very well account (*cf.* the dip and high peak, followed by a second lesser dip and a slight peak, of figs. 5A and 5B) for the peaks at 5050, 5200 and the dips at 5000 and 5110. It should be remembered, in making such comparisons, that the base-line of fig. 2 is largely artificial and depends on the C_0, λ_0 formula, so that "dip" and "peak" are merely relative to neighbouring values, the absolute value of $C - C'$ not entering into the comparison.

In conclusion, although it is not possible to make any positive assertion at this stage, we may at any rate state that the observations, so far as they have gone, do not rule out the hypothesis that these remarkable local irregularities in the curve of photo-elastic dispersion of silica are directly connected with the natural periods of silicon.

[*Note added November 25, 1930.*—The supposition that the local irregularities are due to the natural periods of the element silicon involves the occurrence of this element in the atomic state in vitreous silica. Though this appears *a priori* very unlikely, yet it must be remembered that the effect is brought into existence by stress, and is apparently unconnected with an absorption band of the material in its normal state. It seems therefore not beyond the bounds of possibility that the effect of stress may be to cause a temporary partial dissociation of the molecules of silica, in such a way as to render the free periods of the silicon atoms effective. If, in addition, we bear in mind (*Griffith, 1921) that solids such as glass may contain a multitude of minute crevices, which might well be enlarged, if not actually originated, by stress, free atoms might exist in such crevices. Although we would not be understood to put this forward as a definite hypothesis, the above considerations indicate that the influence of the silicon frequencies is not to be summarily rejected on general grounds.]

BAKERIAN LECTURE.—*The Molecular Structure of Strychnine and Brucine.*

By ROBERT ROBINSON, F.R.S.

(Delivered May 29, 1930.—MS. received January 2, 1931.)

The present position in the development of the chemistry of the strychnos alkaloids has been reached only after much stumbling by the way, and, in view of the confusion which anything but the most attentive study of the whole of the literature must beget, the time seemed ripe for a survey of the salient facts and the statement of the argument which can be based upon them.

Strychnine was isolated from the seeds of *Strychnos Nux-vomica* by Pelletier and Caventou in 1817† and brucine by the same chemists in 1819‡; the composition of these bases was correctly ascertained by Regnault.§

Hanssen|| showed in 1884 that the two alkaloids are closely related, both being convertible by oxidation with chromic acid into an acid, $C_{16}H_{18}O_4N_2$ (old

* 'Phil. Trans.,' A, vol. 221, pp. 163-198.

† 'Berz. Jahresber.,' vol. 1, p. 95 (1817); compare also *ibid.*, vol. 5, p. 237, vol. 8, p. 371.

‡ 'Berz. Jahresber.,' vol. 3, p. 171 (1819).

§ 'Ann. Chem.,' vol. 26, p. 17 (1838).

|| 'Ber. Deuts. Chem. Ges.,' vol. 18, p. 1917 (1885).

formula), but it was the pioneering work of Tafel* which disclosed the main features of the chemistry of the bases, including one of the three important oxidative degradations, and laid down a firm foundation for the labours of his successors. Among these H. Leuchs is pre-eminent and the searching investigations of this chemist and his collaborators have resulted in the discovery of significant step-wise degradations of the molecule by the use of mild reagents and in the accumulation of a mass of cogent data relevant to the constitutional issue. The meticulous accuracy and thoroughness which characterise the fifty-seven memoirs which Leuchs has published (1908-1930) are in accordance with the highest traditions of the German schools of organic chemistry.

In 1909 the late Professor W. H. Perkin initiated a further attack on this difficult problem and the lecturer was privileged to be associated with him in the enterprise; the last few years of Perkin's life were almost wholly devoted to researches on reduced strychnine derivatives in which he displayed his admirable experimental skill to great advantage. It is hoped that the present account will indicate the nature of the progress which was always confidently anticipated by Perkin and a tribute of gratitude and respect is here paid to his memory.

Recently H. Wieland has entered the field, signalling this event by the announcement of the discovery of a new Strychnos alkaloid of the formula, $C_{22}H_{34}O_4N_2$, termed *vomicine*.†

The peculiar complexity of the molecular structure of strychnine and brucine is produced by the fusion of as many as seven rings and this cannot be matched by any other readily accessible natural product; hence the alkaloids are puzzles of a unique character and it is certain that the solution of these must enrich our science both directly and indirectly. A complete elucidation of the whole of the arrangement of atoms in the molecule is not yet possible, but the disposition of five of the associated rings can be deduced from the ascertained facts; the stages of the argument are submitted in the following sections.

* 'Ber. Deuts. Chem. Ges.,' vol. 23, p. 2731 (1890); 'Ann. Chem.,' vol. 264, p. 33 (1891); *ibid.*, vol. 268, p. 229 (1892); *ibid.*, vol. 301, p. 285 (1898); Moufang and Tafel, 'Ann. Chem.,' vol. 304, p. 49 (1899).

† Wieland and Oertel, 'Ann. Chem.,' vol. 469, p. 193 (1929).

The Function of the Nitrogen Atoms in the Strychnine Molecule.

Strychnine is a mono-acid, tertiary base containing neither $\cdot\text{NMe}$ nor $\cdot\text{OMe}$ groups* ; it forms salts such as the hydrochloride, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\cdot\text{H}\}\text{Cl}$, and the methiodide, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\cdot\text{CH}_3\}\text{I}$. The reduction products are also tertiary bases so that the group $-\text{N}=\text{C}:$ is not present. The tertiary basic nitrogen atom is designated N (b). The other nitrogen atom, N (a), is included in a cyclic amide group, $:\text{N}(\text{a})\cdot\text{CO}-$, and its neutral character must be attributed to this circumstance. Tafel† showed that the action of alcoholic sodium ethoxide on strychnine leads to the formation of salts of the imino-carboxylic acid, strychnic acid, $\text{C}_{20}\text{H}_{22}\text{NO}(\text{NH})(\text{CO}_2\text{H})$, which in a gently heated acid solution regenerates the base by dehydration. Strychnic acid gives rise to a nitrosamine, $\text{C}_{20}\text{H}_{22}\text{NO}(\text{N}\cdot\text{NO})(\text{CO}_2\text{H})$. Furthermore the action of alkalis on the strychnine metho-salts furnishes methylstrychnine which is a betaine‡ : $\text{C}_{20}\text{H}_{22}(\text{N}(\text{b})\text{Me})(\text{O})(:\text{N}(\text{a})\cdot\text{CO}\cdot)\}\text{I} + \text{AgOH} \rightarrow \text{C}_{20}\text{H}_{22}(\text{N}(\text{b})\text{Me})(\text{O})(:\text{NH})(\text{CO}_2) + \text{AgI}$. Methylstrychnine can be further methylated yielding methylstrychnic acid methiodide and the action of silver oxide then gives rise to dimethylstrychnine, $\text{C}_{20}\text{H}_{22}(\text{N}(\text{b})\text{Me})(\text{O})(\text{N}(\text{a})\text{Me})(\text{CO}_2)$, or methylstrychnic acid methyl betaine.§ This latter exhibits tertiary basic character and in the formation of dyestuffs simulates N-methyltetrahydroquinoline. Finally, strychnine is reduced in aqueous sulphuric acid solution at a lead cathode to strychnidine, $\text{C}_{31}\text{H}_{24}\text{ON}_2$, and tetrahydrostrychnine, $\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2$, the latter yielding the former under the influence of phosphoryl chloride.|| Now strychnidine is a di-acid, di-tertiary base that suffers no change on treatment with alcoholic sodium ethoxide, and the changes of composition and in properties that have been mentioned indicate that strychnidine is $\text{C}_{20}\text{H}_{22}\text{ON}(\text{N}(\text{a})\cdot\text{CH}_2)$ and tetrahydrostrychnine would then be $\text{C}_{20}\text{H}_{22}\text{ON}(\text{NH})(\text{CH}_2\text{OH})$. This course of the electrolytic reduction of amides is in accord with analogy and has been observed with synthetic compounds of known constitution.

* Shenstone, 'J. Chem. Soc.,' vol. 43, p. 101 (1883) ; vol. 47, p. 139 (1885).

† 'Ann. Chem.,' vol. 204, p. 33 (1891) ; Loebisch and Schoop, 'Monatsh.,' vol. 7, p. 609 (1880).

‡ 'Ber. Deuts. Chem. Ges.,' vol. 23, p. 2731 (1890).

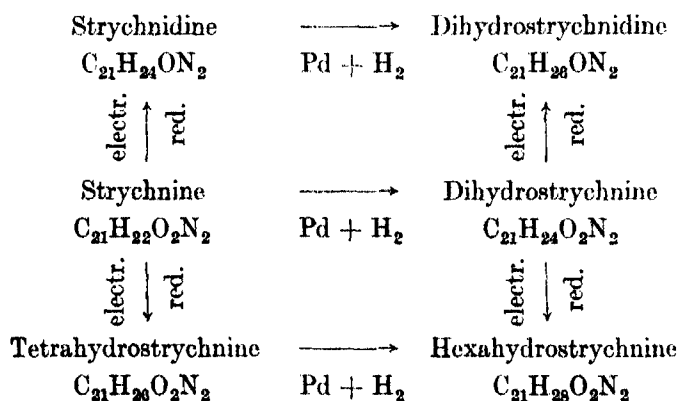
§ Tafel, *loc. cit.*

|| Tafel and Naumann, 'Ber. Deuts. Chem. Ges.,' vol. 34, p. 3291 (1901) ; Tafel, 'Ann. Chem.,' vol. 301, p. 285 (1898).

The Unsaturated Character of Strychnine.

The reduction of strychnine and its simple derivatives by hydrogen in the presence of catalysts discloses the fact that these bases contain one ethylenic linkage.

Thus in presence of palladinised charcoal strychnine, strychnidine and tetrahydrostrychnine are converted into dihydrostrychnine, dihydrostrychnidine-A, and hexahydrostrychnine respectively.* Further electrolytic reduction of dihydrostrychnine furnishes dihydrostrychnidine-A and hexahydrostrychnine, relations that are illustrated in the scheme :

*The Function of the Oxygen Atom of Strychnidine.*

Dihydrostrychnidine-A and the isomeric dihydrostrychnidine-B which is obtained by the prolonged action of boiling hydriodic acid and phosphorus on strychnidine† are quite inactive towards all reagents for the carbonyl and hydroxyl groups and must therefore be ethers. Tafel‡ has shown, however, that oxygen-free bases can be obtained by the application of certain vigorous reduction processes to strychnine without disruption of the molecule. Therefore the ether group is cyclic and the oxygen atom of strychnine not included in the amide group must also possess poly-alkylene oxide function because there is nothing in the nature of the processes necessary for the conversion of strychnine into dihydrostrychnidine which could account for the formation of

* Skita and Franck, 'Ber. Douts. Chem. Ges.,' vol. 44, p. 2863 (1911); Oxford, Perkin and Robinson, 'J. Chem. Soc.,' p. 2389 (1927); Wieland and Münster, 'Ann. Chem.,' vol. 480, p. 39 (1930); Achmatowicz, Fawcett, Perkin and Robinson, 'J. Chem. Soc.,' p. 1769 (1930).

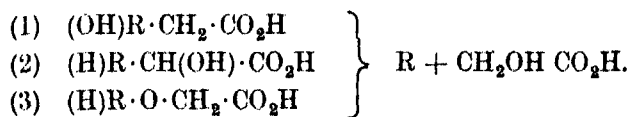
† Perkin and Robinson, 'J. Chem. Soc.,' p. 964 (1929).

‡ 'Ann. Chem.,' vol. 301, p. 285 (1898).

a new ring containing oxygen. Moreover the inert character of the oxygen atom of dihydrostrychnidine is displayed also by that of strychnidine and by one of the oxygen atoms of strychnine. As seen below keto-groups and hydroxyl-groups occurring in strychnine derivatives are not difficult to recognise when they appear in transformation products (compare strychninonic acid, strychnidone, dihydroisostrychnine and many other oxo- and hydroxy-bases and acids). The argument from the behaviour of strychnine and brucine and their simple derivatives appears to be greatly strengthened by the following considerations relating to the Leuchs degradations (*q.v. infra*).

Strychninolic acid, $C_{21}H_{22}O_6N_2$, is obtained from strychnine by means of a permanganate oxidation followed by reduction of the product with sodium amalgam; if it is found to contain an ether group then it will be conceded that strychnine must contain that group also. Now strychninolic acid is a secondary alcoholic monocarboxylic acid which neither *per se* nor in the form of derivatives possesses basic character and thus should contain two :N·CO groups. The acid may therefore be represented by the formula, $C_{17}H_{19}O(N·CO)_2(CH·OH)CO_2H$. Heated with aqueous sodium hydroxide, strychninolic acid is decomposed without hydration or dehydration into strychninolone, $C_{16}H_{16}(N·CO)_2(CH·OH)$, and glycollic acid, $CH_2OH·CO_2H$. The conditions employed were so mild that opening of amide groups by hydrolysis in the course of the process was very improbable and there is no reason to reject the obvious view that the carboxyl of the glycollic acid obtained in the fission is the free carboxyl of strychninolic acid.

The formation of glycollic acid could be represented in the following three ways :—



All these possibilities imply the formation of a double bond or ring in strychninolone not contained in strychninolic acid, and actually it is a double bond that is formed as shown by the course of the oxidation of O-acetylstrychninolone by means of permanganate (Leuchs), and also by the fact that strychninolic acid is unchanged by catalytic hydrogenation, whereas strychninolone yields a dihydro-derivative (unpublished observation).

Scheme (1) is unsupported by analogy unless it be assumed that the group $N·CH_2·CO_2H$ is present in strychninolic acid, and even then the simultaneous dehydration is perplexing in view of the fact that strychninolone does not

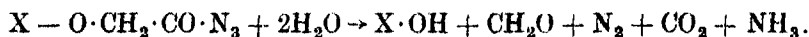
contain the group $C = N$ but rather $C = C$. Further this scheme requires that strychninonic acid should contain a hydroxyl group in addition to a carbonyl group, and there is no evidence that can be adduced in favour of such an assumption. Scheme (2) is likewise highly improbable since, on this basis, strychninolic acid would contain two secondary alcoholic groups, and because strychninolic acid does not exhibit the properties of an α -hydroxy acid.

A by-product in the permanganate oxidation of strychnine is dihydrostrychninonic acid, a stereoisomeride of strychninolic acid capable of further oxidation to strychninonic acid.

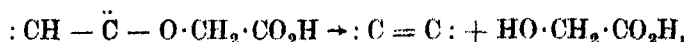
Dihydrostrychninonic acid yields, on treatment with hot dilute aqueous sodium hydroxide, *isostrychninolone*, stereoisomeric with strychninolone and these relations indicate that the secondary alcoholic groups of strychninolic acid and of dihydrostrychninonic acid, which are the cause of the stereoisomerism of these substances, persist unchanged in strychninolone and *isostrychninolone*. Thus in scheme (2) the $-\text{CH}(\text{OH})-$ of the α -hydroxy-acid group is not the group that is oxidised when dihydrostrychninonic acid yields strychninonic acid, and if we accept this scheme it becomes necessary to assume the stability of an α -hydroxy-acid to permanganate under conditions that suffice for the attack of another secondary alcoholic group. Such an assumption offers very great difficulties and hence scheme (2) must be excluded.

There are no objections that can be raised against the adoption of scheme (3) and thus a consideration of the Leuchs degradation affords strong support to the view that strychnine contains an etheric oxygen.

At this stage it may be noted that the Curtius degradation of dihydrobrucinonic acid furnished results* that indicated the occurrence of the group $: \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ or $\cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ in the acid. The decomposition referred to proceeded in the following manner:—



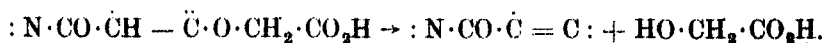
The decomposition,



is in itself an unusual type of reaction and since the double bond formed is not part of a new aromatic nucleus we are forced to believe that the carbonyl groups of the amide systems play a part in facilitating the process.

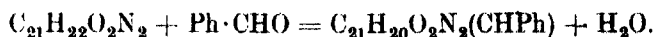
* Leuchs and Kanao, 'Ber. Deuts. Chem. Ges.', vol. 57, p. 1318 (1924).

Thus analogies lead to the view that the significant part of the strychninolic acid to strychninolone decomposition is to be represented by the expression :



The group :N(a)·CO·CH₂·, in Strychnine.

Strychnine (and some of its simple derivatives but not strychnidine) condenses readily with benzaldehyde in alcoholic solution in the presence of potassium hydroxide and affords benzylidenestrychnine.*



Since strychnine contains an ether oxygen atom, the activation of the methylene group cannot be attributed to a keto-group but must be due to the cyclic amide group. It is well-known that oxindole forms arylidene derivatives with ease and cyclic amides, for example N-methylpyrrolidone undergo the Claisen type of condensations with facility. The yellow colour of benzylidene strychnine and of benzylidenebrucine affords an additional argument in favour of our thesis because the group, :N·CO· $\dot{C}$:CHAr, is a weak chromophore in derivatives of cyclic amides.

Therefore strychnine must contain the group :N(a)·CO—CH₂·, which becomes :N·CO· $\dot{C}$:CHPh in the condensation with benzaldehyde.

Strychnine contains a Benzene Ring attached to :N(a)CO·, with an Unsubstituted Position para to N(a).

A comparison of the reactions of strychnine with those of strychnidine clearly proves that the bases stand in the relation of acylaniline derivative to alkylaniline derivative. Thus strychnine is readily halogenated,† sulphonated‡ and nitrated,§ but it does not couple with diazonium salts and it is not oxidised by ferric salts in weakly acidic solution.

On the other hand strychnidine is readily oxidised (like some alkylated tetrahydroquinoline derivatives) by ferric chloride and it couples with diazobenzenesulphonic acid to an azo-compound resembling methyl orange in its

* Perkin and Robinson, 'J. Chem. Soc.,' p. 997 (1929).

† Minunni and Ortoleva, 'Gazz. Chim.,' vol. 30, p. 39 (1900).

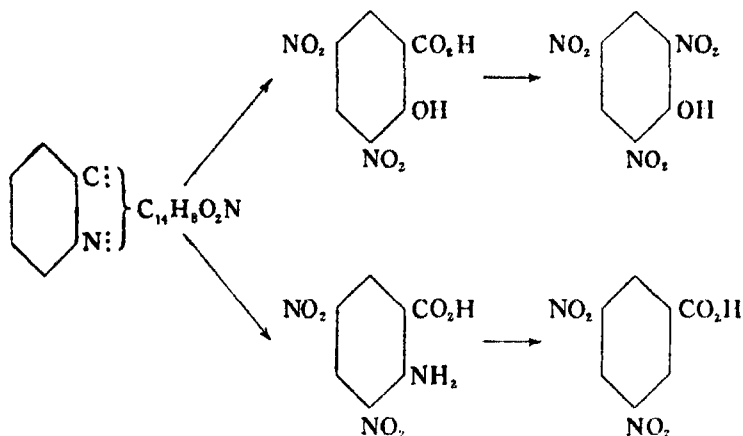
‡ Stöhr, 'Ber. Deuts. Chem. Ges.,' vol. 18, p. 3430 (1885); Leuchs and Schneider, 'Ber. Deuts. Chem. Ges.,' vol. 41, p. 4393 (1908), vol. 42, p. 2681 (1909); Leuchs and Wutke, 'Ber. Deuts. Chem. Ges.,' vol. 45, p. 3686 (1912).

§ Claus and Glassner, 'Ber. Deuts. Chem. Ges.,' vol. 14, p. 773 (1881); Tafel, 'Ann. Chem.,' vol. 301, p. 285 (1898).

indicator properties. More conclusive still, the aminostrychnidine obtained on reduction of the azo-compound simulates *p*-aminodimethylaniline and gives rise to analogues of toluylene blue and toluylene red.*

The betaines methylstrychnine and dimethylstrychnine resemble strychnidine rather than strychnine in these reactions, thus Tafel found that benzaldehyde condensed with dimethylstrychnine to give the leuco-base of a dye of malachite green type.†

The picric acid‡ and 3:5-dinitrobenzoic acid§ that are obtained by the action of hot dilute nitric acid on strychnine clearly owe their formation to the following degradations:—



The reduction of the amino group in the latter reaction is not unique and is paralleled by the formation of nitroanisic acid in a nitric acid oxidation of harmaline. Mention should also be made of other fission products, for example, indole, carbazole and quinoline bases from strychnine|| and methylstrychnine,¶ all at rather high temperatures.

* Oxford, Perkin and Robinson, 'J. Chem. Soc.,' p. 2408 (1927).

† Tafel, 'Ber. Deuts. Chem. Ges.,' vol. 23, p. 2731 (1890).

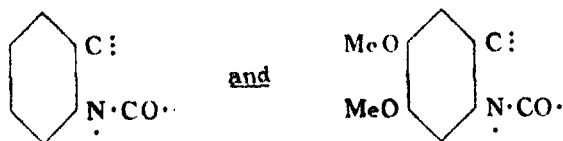
‡ Shenstone, 'J. Chem. Soc.,' vol. 47, p. 139 (1885).

§ Menon, Perkin and Robinson, 'J. Chem. Soc.,' p. 842 (1930).

|| Goldschmidt, 'Ber. Deuts. Chem. Ges.,' vol. 15, p. 1977 (1882); Loebisch and Schoop, 'Monatsh.,' vol. 7, pp. 75, 609 (1886); Stöhr, 'Ber. Deuts. Chem. Ges.,' vol. 20, pp. 810, 1108, 2727 (1887); Loebisch and Malfatti, 'Monatsh.,' vol. 9, p. 626 (1888); Scichilone and Malfatti, 'Gazz. Chim.,' vol. 12, p. 444 (1882).

¶ Clemo, Perkin and Robinson, 'J. Chem. Soc.,' p. 1625 (1927).

Strychnine and Brucine contain respectively the groups



Brucine is dimethoxystrychnine and most of the strychnine chemistry is mirrored in that of brucine; the chief differences are naturally noticed in connection with changes affecting the aromatic nuclei. Hanssen was the first (*loc. cit.*) to demonstrate that by destruction of the aromatic nuclei strychnine and brucine afford one and same acidic product; his work was for a time undeservedly discredited but it has recently been confirmed and elaborated in an elegant manner by Leuchs* and by Wieland.† Thus the molecules of the alkaloids are even configurationally identical apart from the two methoxyl groups.

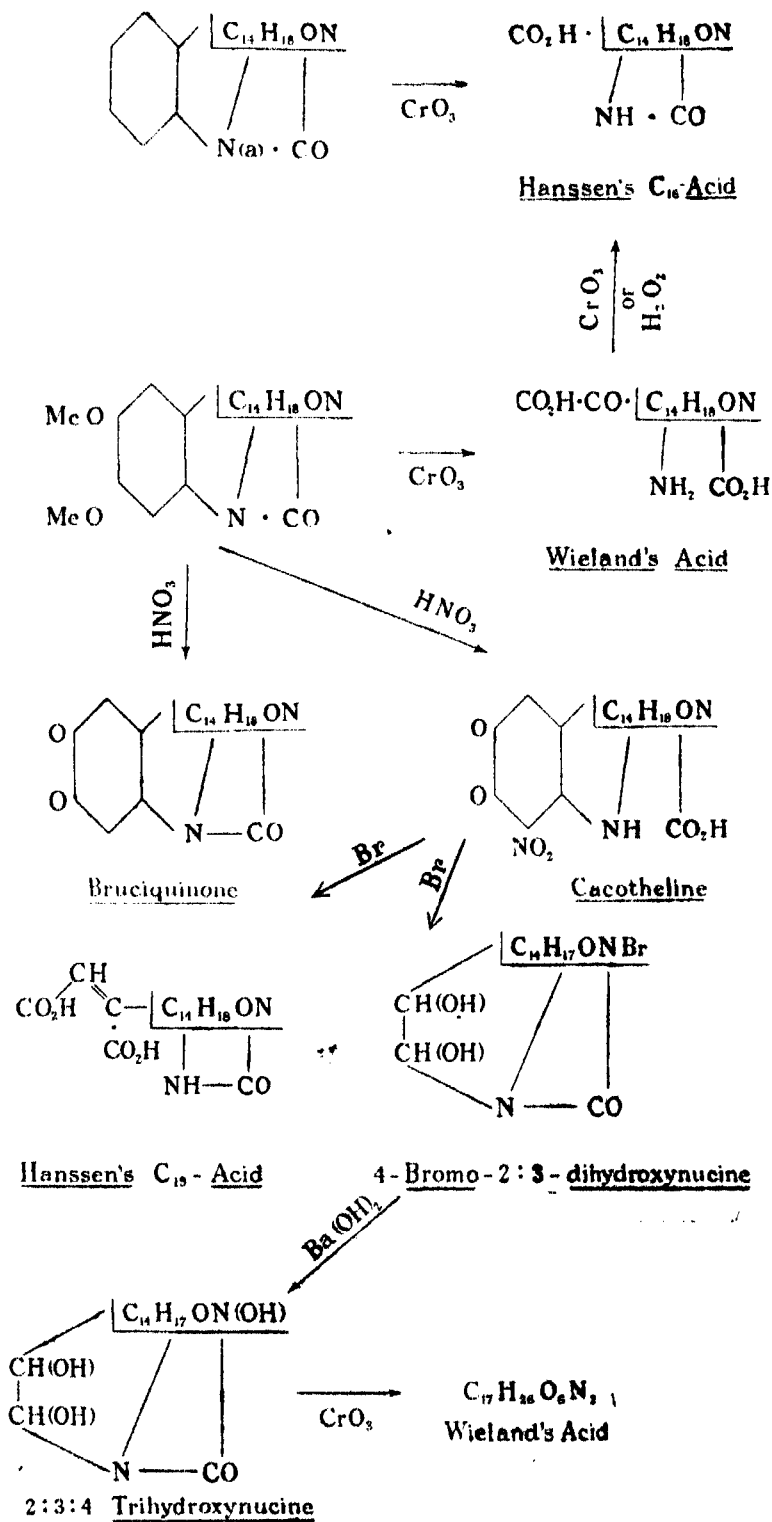
The course of the breaking-up of the ring in brucine by means of nitric acid, bromine, chromic acid and potassium permanganate has been studied in great detail by Leuchs‡ and the following tables illustrate some of the results.

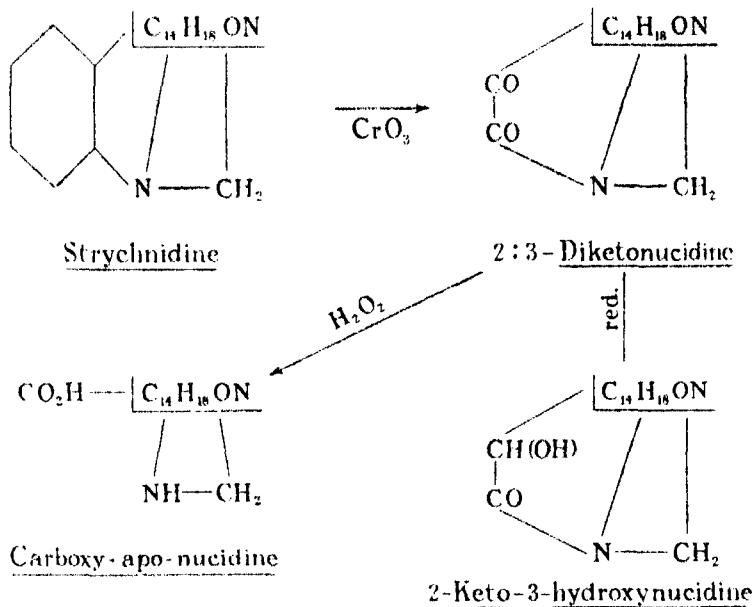
In accordance with a recent suggestion of Leuchs the parent base ($\cdot \text{CO} \cdot \text{N}(a) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot$) ($\text{C}_{13}\text{H}_{18}\text{ON}$) which may hypothetically be derived from strychnine, ($\cdot \text{CO} \cdot \text{N}(a) \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot$) ($\text{C}_{13}\text{H}_{18}\text{ON}$), by removal of four carbon atoms of the benzene ring, is termed *nucine*. *Nucidine* is the related base ($\cdot \text{CH}_2 \cdot \text{N}(a) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot$) ($\text{C}_{13}\text{H}_{18}\text{ON}$).

* Leuchs and Kröhnke, 'Ber. Deuts. Chem. Ges.,' vol. 62, p. 2176 (1929).

† Wieland and Münster, 'Ann. Chem.,' vol. 469, p. 216 (1929); Cortese, 'Ann. Chem.,' vol. 476, p. 280 (1929).

‡ Leuchs and Geiger, 'Ber. Deuts. Chem. Ges.,' vol. 42, p. 3067 (1909); Leuchs and Weber, 'Ber. Deuts. Chem. Ges.,' vol. 42, p. 3703 (1909); Leuchs, Mildbrand and R. Leuchs, 'Ber. Deuts. Chem. Ges.,' vol. 55, p. 2703 (1922); compare Hanssen, 'Ber. Deuts. Chem. Ges.,' vol. 20, p. 452 (1887), and Ciusa and Scagliarini, 'Atti. R. Accad.,' Lincei, vol. 19, p. 504 (1910); Leuchs and Taube, 'Ber. Deuts. Chem. Ges.,' vol. 57, p. 1092 (1924); Leuchs, 'Ber. Deuts. Chem. Ges.,' vol. 58, p. 1730 (1925); Leuchs, Bender and Wegener, 'Ber. Deuts. Chem. Ges.,' vol. 61, p. 2353 (1928); Leuchs, 'Ber. Deuts. Chem. Ges.,' vol. 62, p. 1929 (1929); Leuchs and Hofmann, 'Ber. Deuts. Chem. Ges.,' vol. 62, p. 2307 (1929), vol. 63, p. 440 (1930).





There are many further transformations; thus the maleinoid group of the Hanssen C_{10} -acid may be saturated or degraded by oxidation with formation of oxalic acid. Many of the nucine and nucidine derivatives may be oxidised by bromine water at the original strychnine double bond in the $C_{14}H_{18}ON$ complex; the products are aldehydes capable of further oxidation to acids by means of yellow mercuric oxide. This confirms the presence of the group, $—CH = X$, in strychnine (compare, however, the section, *Adverse Considerations*, below).

The position of the methoxyl groups in brucine has been deduced as the result of a comparison* of the colour-reaction of the base and nitric acid with those exhibited by various synthetic N-acetyldimethoxydimethyltetrahydroquinolines in like circumstances. This comparison was decisive in favour of the formulæ given above in the text.

Dinitrostrychnolcarboxylic Acid and its Degradation to Dinitroisatin.

The first action of hot dilute nitric acid on strychnine is the formation of nitrostrychnine† and then of dinitrostrychnine hydrate,‡ a carboxylic acid capable of esterification§ $\{Ar \cdot N(a) \cdot CO \cdot \rightarrow (NO_2)_2Ar \cdot NH \cdot CO_2H\}$; subse-

* Lions, Perkin and Robinson, 'J. Chem. Soc.', vol. 127, p. 1158 (1925).

† Loebisch and Schoop, 'Monatsh.', vol. 6, p. 845 (1885).

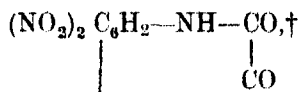
‡ Claus and Glassner, 'Ber. Deuts. Chem. Ges.', vol. 14, p. 774 (1881).

§ Tafel, 'Ann. Chem.', vol. 301, p. 285 (1898).

quently oxidation occurs and the chief product is dinitrostrycholcarboxylic acid, $C_9NH_2(NO_2)_2(OH)_2CO_2H$.*

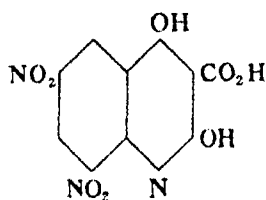
The groups indicated in this expression have been recognised by some of the usual methods, the carboxyl group by expulsion of carbon dioxide yielding dinitrostrychol, $C_9NH_3(NO_2)_2(OH)_2$, the nitro-groups by reduction to amino-groups, one phenolic hydroxyl group by ether formation, whilst barium dinitrostrycholate appears to have the composition, $C_9NH_3(NO_2)_2(O_2Ba)$ indicating a second hydroxyl group. The hypothetical parent substance *strychol* has the composition of a dihydroxyquinoline or dihydroxyisoquinoline and clearly one of the so-called hydroxyl groups may be in the tautomeric $-NH \cdot CO-$ system.

The esterification of dinitrostrycholcarboxylic acid with ethyl alcohol and sulphuric acid introduces two ethyl groups yielding ethyl dinitro-*O*-ethylstrycholcarboxylate, $C_9NH_2(NO_2)_2(OH)(OEt)CO_2Et$ and application of the Curtius reaction to this ester furnished the urethane, $C_9NH_2(NO_2)_2(OH)(OEt)NH \cdot CO_2Et$, which in its turn by hydrolysis and oxidation by acid permanganate afforded dinitroisatin,

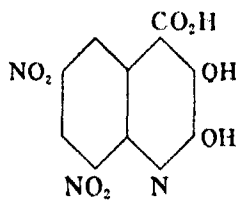


which is oxidised by nitric acid to picric acid.

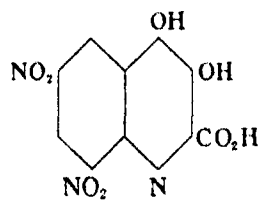
This transformation clearly proved that strychol is a dihydroxyquinoline (or tautomeride) with both hydroxyls in the pyridine nucleus, and the following formulæ for dinitrostrycholcarboxylic acid alone call for consideration.



(I)



(II)



(III)

It is possible to replace the carboxyl group by nitroxyl and thus obtain trinitrostrychol, $C_9NH_2(NO_2)_3(OH)_2$.

According to (I) this substance should be 3 : 6 : 8-trinitro-2 : 4-dihydroxy-

* Leuchs and Hintze, 'Ber. Deuts. Chem. Ges.', vol. 52, p. 2204 (1919); Leuchs and Kröhnke, 'Ber. Deuts. Chem. Ges.', vol. 62, p. 2176 (1929).

† Menon, Perkin and Robinson, *loc. cit.*

quinoline but a compound of this constitution was synthesised and found to differ from trinitrostrychol.*

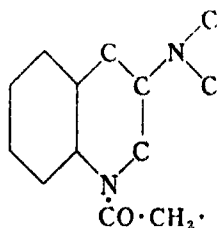
More recent as yet unpublished synthetic work also appears to exclude the formula II and to indicate that III is correct but the decision between these alternatives is not material for the purposes of the present discussion.

Conclusions from the Results of the Nitric Acid Oxidation. Position of N(b) relative to N(a).

The deduction from the foregoing section is that strychnine is a quinoline derivative and the recorded formation of indole from strychnine does not militate against this view because several instances of the ready production of indole from quinoline derivatives have been placed on record. Accepting this, it seems quite natural that the α - or γ -positions in the pyridine nucleus should bear hydroxyls in the nitration oxidation product, but the hydroxyl in the β -position, common to formulæ II and III, is curiously situated and a special explanation of its origin appears to be called for.

It might mark the position of the ether oxygen in the strychnine molecule, but a few trials will show that this is an unworkable proposition and the pieces have not been found to fit together on this basis.

The alternative that the hydroxyl in the β -position is a relic of N(b) is adopted as a working hypothesis; it leads without further assumptions to the part skeleton :



Here the α -position in the quinoline ring cannot be the site of the —N(a)·CO— group because we have seen that this group may be expanded to $\text{—N(a)·CO·CH}_2\text{—}$.

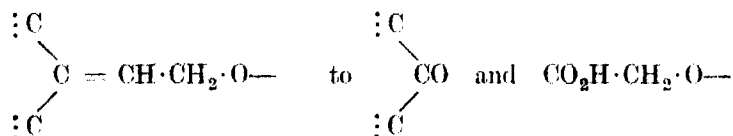
The Leuchs Degradation.†

Oxidation of strychnine by means of potassium permanganate in acetone solution affords strychninonic acid, $\text{C}_{21}\text{H}_{20}\text{O}_6\text{N}_2$, dihydrostrychninonic acid,

* Ashley, Perkin and Robinson, 'J. Chem. Soc.,' p. 382 (1930).

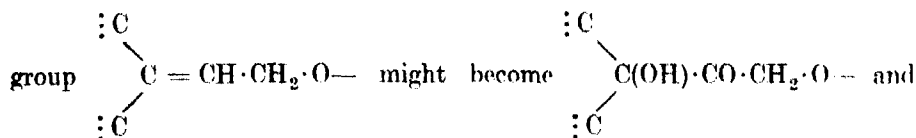
† Leuchs, 'Ber. Deuts. Chem. Ges.,' vol. 41, p. 1711 (1908); Leuchs and Schneider, 'Ber. Deuts. Chem. Ges.,' vol. 41, p. 4393 (1908); vol. 42, p. 2494 (1909); Leuchs and Weber, *ibid.*, p. 3703; Leuchs and Reich, 'Ber. Deuts. Chem. Ges.,' vol. 43, p. 2417 (1910);

$C_{21}H_{22}O_6N_2$, and a number of other substances in small relative proportion. Strychninonic acid is a ketone (semicarbazone, oxime, reduction to secondary alcoholic strychninolic acid, $C_{21}H_{22}O_6N_2$) and a mono-carboxylic acid (esters). Leuchs was long of the opinion that it was a dicarboxylic acid, but all attempts to prove this failed, and a second carboxyl group could only be demonstrated after the addition of a molecule of water; evidently due to the hydrolysis of an amide group. It is saturated to permanganate and reasons have already been advanced for the belief that it contains the group $C-O-CH_2\cdot CO_2H$. Its esters have no basic character and we therefore assume two $-N\cdot CO-$ groups. The acid may be written $C_{16}H_{17}(N\cdot CO)_2(CO)\cdot O\cdot CH_2\cdot CO_2H$, and it must be formed from strychnine by the oxidation of

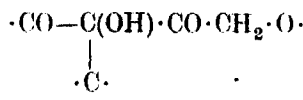


and by oxidation of $-N(b)\cdot CH_2-$ to $-N(b)\cdot CO-$.

The formation of dihydrostrychninonic acid is very interesting and there are two possible explanations of it each leading to the same conclusion. The



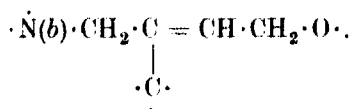
then suffer hydrolytic fission; in accordance with experience this would be an improbable reaction unless the system were



when it would be plausible. The carbonyl group to the left could not be that of $\cdot N(a)\cdot CO\cdot$ because this is joined to a methylene group and therefore it should be the newly formed carbonyl of the $-N(b)\cdot CO-$ system.

Leuchs and Brewster, 'Ber. Deuts. Chem. Ges.,' vol. 45, p. 201 (1912); Leuchs and Peirce, *ibid.*, pp. 2653, 3412; Leuchs and Rauch, 'Ber. Deuts. Chem. Ges.,' vol. 47, p. 370 (1914); Leuchs, *ibid.*, p. 536; Leuchs and Schwaebel, 'Ber. Deuts. Chem. Ges.,' vol. 47, p. 1552 (1914), vol. 48, p. 1009 (1915); Leuchs and Bendixsohn, 'Ber. Deuts. Chem. Ges.,' vol. 52, p. 1443 (1919); Leuchs and Ritter, *ibid.*, p. 1583; Leuchs, Hellriegel and Heering, 'Ber. Deuts. Chem. Ges.,' vol. 54, p. 2177 (1921); Leuchs and Nitschke, *ibid.*, p. 3738; Leuchs, Gladkorn and Hellriegel, 'Ber. Deuts. Chem. Ges.,' vol. 56, p. 2472 (1923); Leuchs, 'Ber. Deuts. Chem. Ges.,' vol. 62, p. 407 (1929).

Alternatively we might suppose the oxidation to go to the stage $\cdot\dot{N}(b)\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot$ and the alcoholic group to be then formed by an oxidation-reduction process. In either case we find that strychnine contains the group



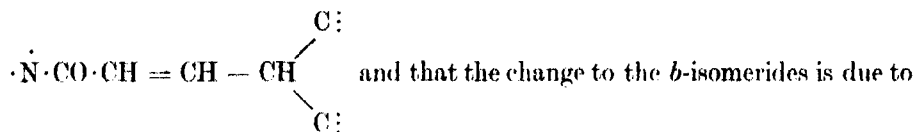
This view of the relation of N(b) to the unsaturated centre is supported by other considerations mentioned below.

Exactly corresponding to strychninonic acid and strychninolic acid are brucinonic acid and its reduction product brucinolic acid, $(\text{MeO})_2\text{C}_{16}\text{H}_{15}(\text{N}\cdot\text{CO})_2(\text{CH}\cdot\text{OH})\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and this latter is decomposed in hot alkaline solution yielding brucinolone, $(\text{MeO})_2\text{C}_{16}\text{H}_{14}(\text{N}\cdot\text{CO})_2(\text{CH}\cdot\text{OH})$, and glycollic acid.

The strychninolone and brucinolone first produced are labile, being converted by the action of basic catalysts, for example, methyl alcoholic ammonia, into isomerides.

In the strychninolone series the first product is strychninolone-*a*; this passes readily into strychninolone-*b* and with more difficulty into strychninolone-*c*. In the brucine series the corresponding isomerides are brucinolones-*a* and *b* and cryptobrucinolone; isobrucinolone is derived from dihydrobrucinonic acid.

Leuchs has clearly demonstrated that the *a*-isomerides contain the group



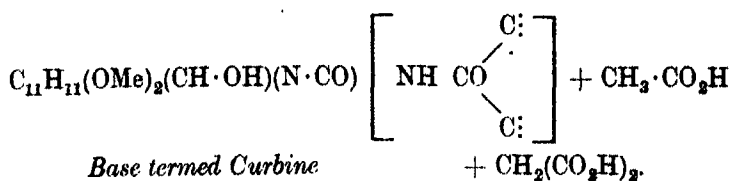
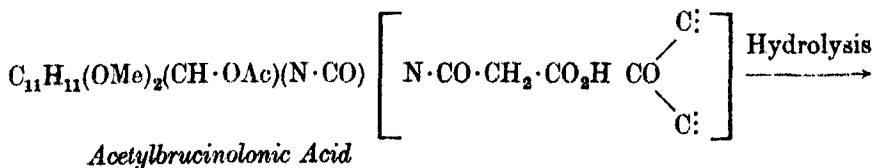
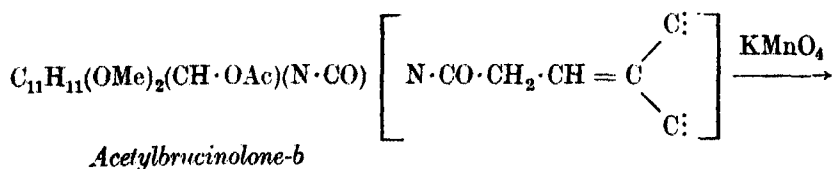
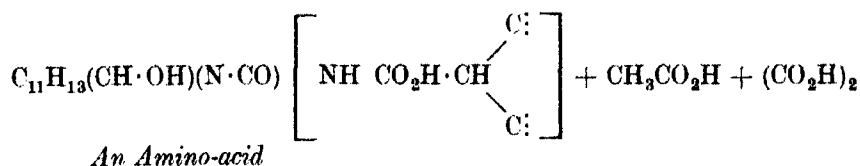
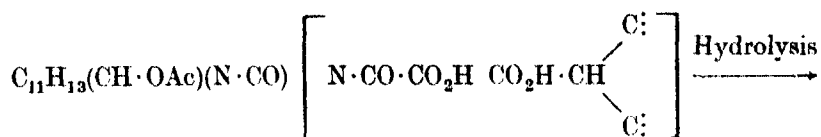
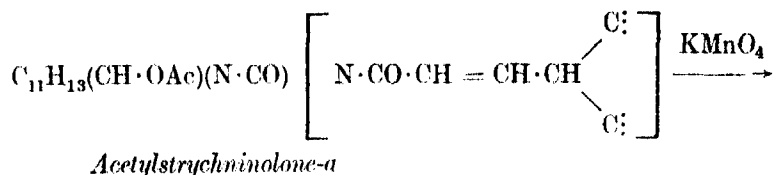
the wandering of the double bond giving the system $\cdot\dot{N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}=\underset{\text{C}\vdots}{\overset{\text{C}\vdots}{\text{C}}}$.

The formation of strychninolone-*c* and of cryptobrucinolone involves a return of the double bond to its original position and some other change must occur in the molecule.

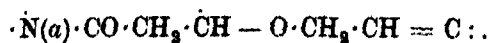
The change from strychninolone-*a* to strychninolone-*b* proves that the $\beta\gamma$ -phase of the so-called three carbon system possesses considerable stability, and this is in harmony with the results of recent researches of Kon and Linstead who have indicated the factors influencing the equilibrium and among them found that alkyl-substitution of the γ -position favours the $\beta\gamma$ -form.

Leuchs oxidised the O-acetyl-derivatives of the strychninolones and bruci-

nolones and the following two examples will serve to illustrate the nature of the evidence so obtained.



Obviously if the earlier deductions respecting the relation of N(b) to the unsaturated linkage of strychnine are sound it follows that the N·CO in the right-hand bracket in the above formulæ must be N(a)·CO. The mobile double bond is certainly that produced when glycollic acid is eliminated from strychninolic acid so that it is necessary to assume that strychnine contains the group



The ether oxygen cannot be attached in the α -position (benzylidenestrychnine) and attachment to the γ -position is improbable since strychninolone-a is the primary product of the decomposition of strychninolic acid.

Further Evidence bearing on the Propinquity of the Ether Oxygen and N(a)CO in the Molecular Structure.

The ether oxygen in strychnidine is remarkably firmly held but in strychnine it enters into several transformations and this contrast argues a close connection of N(a)·CO and the ether oxygen atom in the molecule.

Thus under the influence of basic catalysts strychnine and dihydrostrychnine yield respectively *isostrychnine** and dihydro*isostrychnine*.† It is possible to show by the formation of O-acyl-derivatives‡ that these bases contain an alcoholic hydroxyl group and this can only be derived by scission of the oxide ring.

The reaction is not yet fully understood but the implication of N(a)·CO in the process is clearly indicated by the fact that neither *isostrychnine* nor dihydro*isostrychnine* can be condensed with benzaldehyde.§ N(a)·CO remains (*isostrychnic acid*) so that it is the attached methylene group that is modified.

Again, whereas strychnidine on reduction with hydrogen iodide and phosphorus yields only dihydrostrychnidine-B the ether oxygen remaining intact, strychnine affords under these conditions desoxystrychnine by removal of the ether oxygen and further reduction : $C_{21}H_{22}O_2N_2 + 6H = C_{21}H_{26}ON_2 + H_2O$. Desoxystrychnine still contains ·N (a)·CO as shown by its colour reactions, its mono-acidic tertiary basic character, its hydrolysis to desoxystrychnic acid and its reduction at a lead cathode to dihydrostrychnoline, $C_{21}H_{28}N_2$.|| To derive its formula from that of strychnine we replace the ether oxygen by two hydrogen atoms and saturate the double bond.

Further Evidence bearing on the Relation of N(b) to the Ethylene Linkage of Strychnine.

The metho-salts of strychnine and strychnidine and of their dihydro-derivatives and the brucine analogues of these substances react with sodium

* Tafel, 'Ann. Chem.,' vol. 264, p. 33 (1891); Bacovescu and Pictet, 'Ber. Deuts. Chem. Ges.,' vol. 38, p. 2787 (1905); Leuchs and Nitschke, 'Ber. Deuts. Chem. Ges.,' vol. 55, p. 3171 (1922).

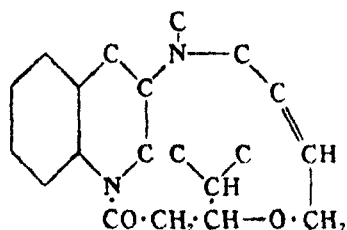
† Oxford, Perkin and Robinson, *loc. cit.*

‡ Ciusa, 'Atti. R. Acad., Lincei,' vol. 28, p. 185 (1919), and Oxford and others, *loc. cit.*

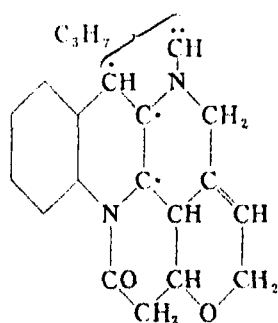
§ Achmatowicz, Davies, Perkin and Robinson (unpublished).

|| Tafel, 'Ann. Chem.,' vol. 268, p. 229 (1892), vol. 301, p. 285 (1898).

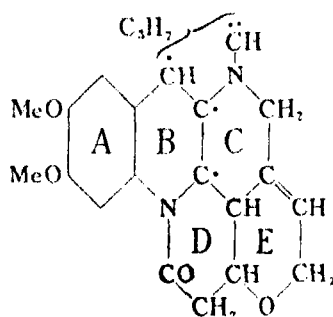
These may be combined in the following manner :



Two of the carbon atoms in this structure are superfluous and on removing them an expression with five fused rings is obtained ; to this we may safely add two hydrogen atoms giving the annexed formulæ for strychnine and brucine. There is definite evidence of the CH group in position-4 of nucine (see above).



Strychnine.



Brucine.

There is no evidence of the disposition of the atoms of the group C_3H_7 but they must be added so as to introduce two new rings because the alkaloids contain only one double bond.

There is no difficulty in constructing a number of the possibilities, bearing in mind the probable similarity of the skeletons of cinchonine and strychnine and the desirability that the model based on the formula shall be unstrained. It is not, however, the object of the present discussion to stray into these regions of speculation.

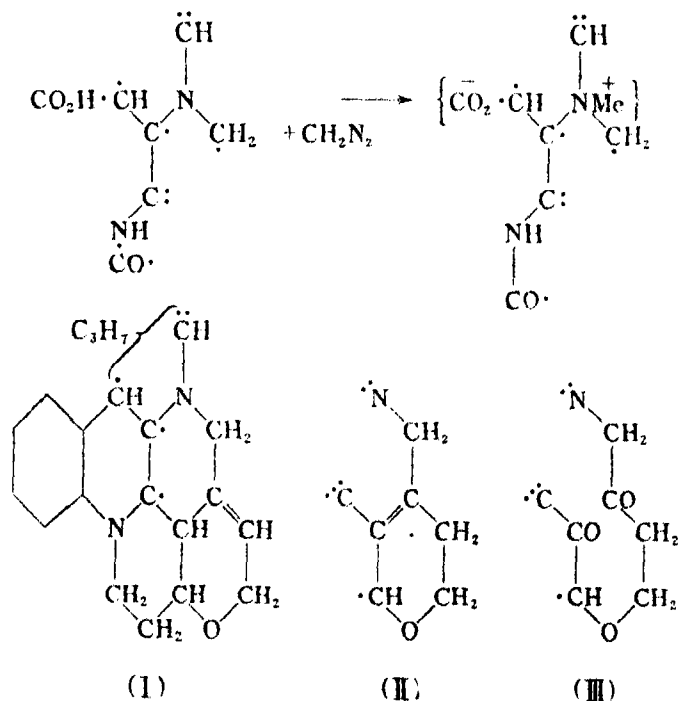
Nevertheless it is found that the approximate shape and dimensions of the discoid molecules, as estimated from the various models of particular formulæ based on the general expression, do not vary over a wide range.

The lecturer is very much indebted to Miss T. C. Marwick, who examined by X-ray methods crystals of strychnine prepared by Miss H. Gilchrist, and reported that the unit cell contained four molecules and that the dimensions

of the cell were such that four molecules of the shape and size suggested by one of the more plausible formulæ could be conveniently accommodated in it.

In the foregoing development no attempt has been made to cover the whole field of the chemistry of these alkaloids, although it is believed that the proposed structures adequately summarise what is certainly ascertained in regard to them. Investigations made since the formulæ were propounded have provided confirmatory evidence and two examples may be cited in conclusion.

It has been found that the Haussen- C_{16} Acid cannot be esterified in the usual manner in that the alkyl group passes to N (b) with formation of a betaine.* This shows that the carboxyl group and N (b) are close to one another in the molecule. The relation of the carboxyl in question to N (b) on the basis of the new strychnine formula is shown in the part scheme :—



The second case† is provided by the discovery that the compound previously called methyl- ψ -strychnidine is really isomeric with strychnidine and may be termed *neostrychnidine*. On oxidation it is known to yield strychnidone,‡

* Wieland and Münster, 'Ann. Chem.,' vol. 480, p. 39 (1930).

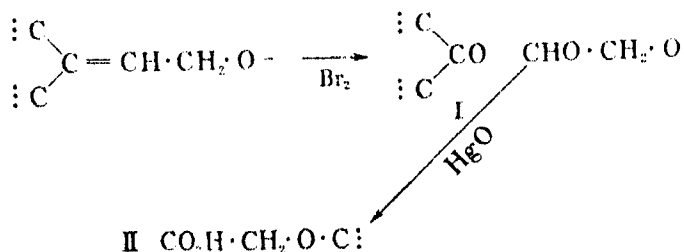
† Achmatowicz, Perkin and Robinson, forthcoming publication.

‡ Clemo, Perkin and Robinson, *loc. cit.*

a diketone. The change of strychnidine (I) to *neostrychnidine* (II) and strychnidine (III) is explicable as illustrated and the assumption that *neostrychnidine* differs from strychnidine only in the position of the double bond is rendered necessary by the observation that catalytic reduction of *neostrychnidine* yields dihydrostrychnidine-A identical with the product from strychnidine.

Adverse Considerations.—(1) It can be argued that the formulæ advocated do not explain the noticeable effect of the double bond on the stability of the lactam ring. For example dihydrostrychnine cannot be hydrolysed to dihydrostrychnic acid and in general the amide group in all the reduced derivatives is characterised by resistance to hydrolytic fission. The answer to this objection may be that ring D (see brucine formula above), the strain or stability of which is under consideration, is fused to rings C and E each of which include atoms of the double bond. The strain in C and E should be changed when the double bond is saturated, and as the researches of Thorpe and of Mills have proved this would have a profound effect on the strain in the fused ring D and therefore on the chemical properties that it evinces. A second line of reply is that the factors controlling the opening of the lactam ring are not apparent in other cases. Thus the Wieland-C₁₇-acid is hydrated at the N (*a*)·CO group but the Hanssen-C₁₆-acid, so closely related, contains the amide group of strychnine.

(2) The many cases in which Leuchs and his co-workers have oxidised strychnine derivatives with bromine water adding 2O with formation of an aldehyde and subsequently forming the corresponding acid by the action of mercuric oxide are interpreted on our basis by the scheme.

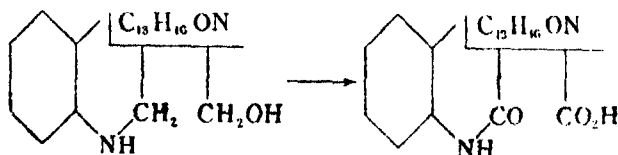


The carbonyl group represented (I) has not been experimentally recognised, but it cannot be that N (*b*)·CO is produced in the oxidation by means of bromine water because the substances retain basic character. It is not unusual however for basic ketones to exhibit sluggish carbonyl reactivity, a good example being cryptopine. Then again Leuchs has found that a sub-

stance supposed on the present basis to contain the ether group (II) is stable to boiling concentrated aqueous hydrobromic acid.

Still it is not certain that such an ether ought to be expected to undergo hydrolysis under these conditions. The substance is basic and hydrolysis of the ether group presupposes the formation of an oxonium salt of a substance already containing an ammonium group. When it is considered that the ratio of the first to the second dissociation constant of a di-acid base is always high and that this will be exaggerated in the case of an oxonium base following an ammonium one, and, finally, that after all it is an ether group that is being considered, it need not occasion surprise that the substance remained unattacked.

(3) Very recently* Leuchs has described the oxidation of tetrahydrostrychnine by chromic acid to an amino-acid, $C_{21}H_{22}O_4N_2$, and other products. Here apparently the change is interpreted in accordance with the scheme :



It seems equally possible that a group : N(a)CH· $\ddot{O}$ ·CH· might give : N(a)·CO and : C = C· which changes could be accommodated and would limit the possible modes of attachment of the unassigned C_3H_7 groups. The further development of this novel attack will be awaited with interest, and if Leuchs' interpretation is correct the skeleton given above at the top of p. 449 must be developed with a bridge across the quinoline ring,

Appendix.—In December, 1930, Späth and Bretschneider† published a paper in which the oxidation of strychnine to N-oxalylanthranilic acid and of brucine to 4 : 5-dimethoxy-N-oxalylanthranilic acid is described. The former result does not add to the information already available from the degradation of dinitrostrycholcarboxylic acid to dinitroisatin, but the latter result is a welcome confirmation of Leuchs' view that the methoxy groups of brucine are in the *o*-position and of our assignment of the 6 : 7-position in the quinoline nucleus to these groups.

* 'Ber. Deuts. Chem. Ges.,' vol. 63, p. 3184 (1930).

† 'Ber. Deuts. Chem. Ges.,' vol. 63, p. 2997 (1930).

Physical Constants of the System Methane-Hydrogen.

By F. A. FREETH, F.R.S., and T. T. H. VERSCHOYLE.

(Received June 14, 1930.)

§ 1. *Introduction.*

Isotherms of methane have been determined for a series of temperatures between 0° and 200° C. by Keyes, Smith, and Joubert,* and by Keyes and Burks,† but, inasmuch as the highest pressure reached at 0° in these researches was 130 atmospheres, and the isotherm as extrapolated from their derived equation did not indicate the expected pv_A minimum at about 150 atmospheres (*vide* § 3), it was deemed advisable to extend the measurements at 0° to 220 atmospheres, and also to determine the isotherm at 20° C.

Olszewski‡ was the first to measure the vapour pressures of methane, down to a temperature of -203° C., but his results are chiefly of historical interest. Determinations of the vapour pressures of the liquid between -182° and -150° C. have been made by Stock, Henning, and Kuss,§ but, apart from a solitary measurement of the triple-point by Crommelin,|| no modern work seems to have been done on the vapour pressures of the solid. The range between -178° and the critical temperature has been covered by Keyes, Taylor, and Smith¶ in a comprehensive paper upon the thermodynamic properties of methane.

No investigation appears to have been made on the melting-point curve. Furthermore, there is no record of any research on the binary system methane-hydrogen.

§ 2. *Experimental Methods.*

The isotherms at normal temperatures were measured by the method already described in detail by one of us.** A full account of the methods of determination of the vapour pressures, of the melting-point curve, of the three-phase curve, and of the low-temperature isotherm will be published shortly in an account

* 'J. Math. Phys. Mass. Inst. Techn.,' vol. 1, p. 191 (1922).

† 'J. Amer. Chem. Soc.,' vol. 49, p. 1403 (1927).

‡ 'C. R.,' vol. 100, p. 940 (1900).

§ 'Ber. Deuts. Chem. Ges.,' vol. 54, p. 119 (1921).

|| 'Phys. Lab. Leiden, Commn.,' No. 131b.

¶ 'J. Math. Phys. Mass. Inst. Techn.,' vol. 1, p. 211 (1922).

** Verschoyle, 'Proc. Roy. Soc.,' A, vol. 111, p. 552 (1926).

of the ternary system carbon monoxide-nitrogen-hydrogen, and it is therefore not proposed to repeat it here.

Two processes were employed for the preparation of the methane : first, the action of water on magnesium methyl iodide, and, secondly, the action of heat on a mixture of soda-lime and dehydrated sodium acetate. The crude gas evolved in the former process was passed through two traps cooled by solid carbon dioxide and alcohol, and condensed in liquid air. The condensate was then submitted to four successive fractionations at a pressure of about 1 cm. of mercury, with the aid of a small heating-coil to ensure regular ebullition, only the middle fraction being collected in each operation after passage through a filter-spiral immersed in liquid air. This sample was used for the vapour pressure work only.

For all the other investigations the product of the second process was used, and this, which is the method adopted by Keyes and his collaborators, is undoubtedly the most satisfactory of all the reactions hitherto suggested. The gas was subjected to a chemical purification by passage through fuming sulphuric acid, ordinary sulphuric acid, and caustic potash solution, and it was then fractionally distilled six times in succession, the process being controlled by the use of a glass bell to entrap some of the vapour phase. After the fifth fractionation, the vapour phase collapsed completely, no excess pressure being required.

§ 3. *Isotherms at 0° and 20° C.*

Control determinations of the isotherm of hydrogen at 20° C. were carried out both before and after the methane series. It was found that the resistance-volume factor of the piezometer stem wire was not so regular as it had been during the work on hydrogen and nitrogen (*loc. cit.*), and all observations were, therefore, made with approximately the same set of values of the resistance of the stem wire, individual mean corrections for each value being derived from the two control series and applied to the methane series. The agreement between the control series was not particularly good, especially (and unfortunately) for small volumes, so that the accuracy of the isotherms is probably not better than 1 in 500.

Two series were measured at each temperature, the normal volumes being respectively about 300 and 900 cm.³. The results are contained in Tables I and II, and those points for which the volume correction was rather uncertain are marked with asterisks ; in deriving the equations for the isotherms, these points have been given only half the weight of the others. The volume (v_A) is expressed in terms of the normal volume.

Table I.—Isotherm at 0° C.

Point.	p atms.	pv_A (obs.).	pv_A (calc.).	$O - C.$
I 1	23.54	0.9433	0.9456	-0.0023
2	33.16	0.9200	0.9228	-0.0028
II 1	46.99	0.8918	0.8902	+0.0016
I 3	49.56	0.8829	0.8844	-0.0015
4*	64.05	0.8506	0.8519	-0.0013
II 2	67.14	0.8454	0.8449	+0.0005
I 5*	72.76	0.8354	0.8335	+0.0019
II 3	91.33	0.7984	0.7978	+0.0006
4	113.52	0.7647	0.7642	+0.0005
5	133.83	0.7454	0.7446	+0.0008
6	171.55	0.7415	0.7409	+0.0006
7*	179.29	0.7429	0.7452	-0.0023
8*	215.10	0.7775	0.7776	-0.0001

Mean error of observation = ± 0.0016 .

Table II.—Isotherm at 20° C.

Point.	p atms.	pv_A (obs.).	pv_A (calc.).	$O - C.$
I 1	17.19	1.0399	1.0396	+0.0003
2	25.47	1.0228	1.0231	-0.0003
3	35.10	1.0039	1.0044	-0.0005
II 1	38.84	0.9990	0.9974	+0.0016
2	51.28	0.9770	0.9750	+0.0020
I 4	53.42	0.9711	0.9713	-0.0002
5*	69.85	0.9428	0.9443	-0.0015
II 3†	74.39	0.9417	0.9373	+0.0044
I 6*	79.53	0.9309	0.9297	+0.0012
II 4	99.97	0.9008	0.9028	-0.0020
5	128.03	0.8740	0.8750	-0.0010
6	151.24	0.8637	0.8621	+0.0016
7*	195.74	0.8720	0.8703	+0.0017
8*	205.41	0.8773	0.8792	-0.0019

† Point II (3) has been omitted in deriving the equation, for its error appears unaccountably large.

Mean error of observation = ± 0.0014 .

On plotting the experimental values of pv_A , it was evident that the isotherm could not be satisfactorily represented by the usual three-constant equation, but that a fourth term would be necessary. In the case of the isotherm at 20° C. a satisfactory expression of the usual form

$$pv_A = A_p + B_p p + C_p p^2 + D_p p^4$$

could be obtained, but for the isotherm at 0° C., a higher power of p was requisite :—

$$pv_A = A_p + B_p p + D_p p^4 + E_p p^6.$$

The equations which, derived by the method of least mean squares, best represent the isotherms are :—

$$pv_A = 1.0024 - 2.411 \times 10^{-3}p + 2.428 \times 10^{-10}p^4 - 2.282 \times 10^{-15}p^6 \quad \dots\dots\dots 0^\circ \text{ C.}$$

$$pv_A = 1.0758 - 2.177 \times 10^{-3}p + 4.005 \times 10^{-6}p^2 + 4.582 \times 10^{-11}p^4 \quad \dots\dots\dots 20^\circ \text{ C.}$$

The curves representing these equations and the experimental points are plotted in figs. 1 and 2. The relation between the pressure and the value of the mean expansion coefficient between 0° and 20° C. is reproduced in fig. 3.

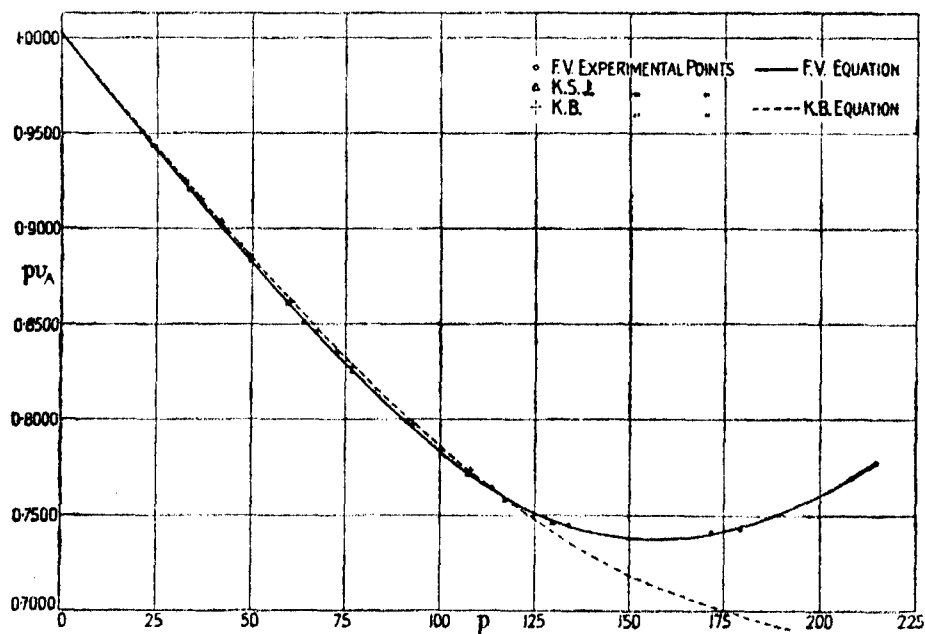


FIG. 1.—Methane Isotherm at 0° C.

In addition to our results (F.V.), fig. 1 also contains the experimental observations of Keyes, Smith, and Joubert (K.S.J.)* and of Keyes and Burks (K.B.),† and, furthermore, a curve drawn through points calculated from the general equation of state for methane derived by the latter authors. From an inspection of the curves some interesting conclusions may be drawn. First, the K.S.J. experimental data agree very closely with our own, and, although the agreement with the K.B. data is not quite so good, yet the largest deviation does not exceed 1 in 350.

* *Loc. cit.*

† *Loc. cit.*

Secondly, the isotherm for 0°C . derived from the K.B. equation of state, whilst representing the observational results reasonably well up to pressures

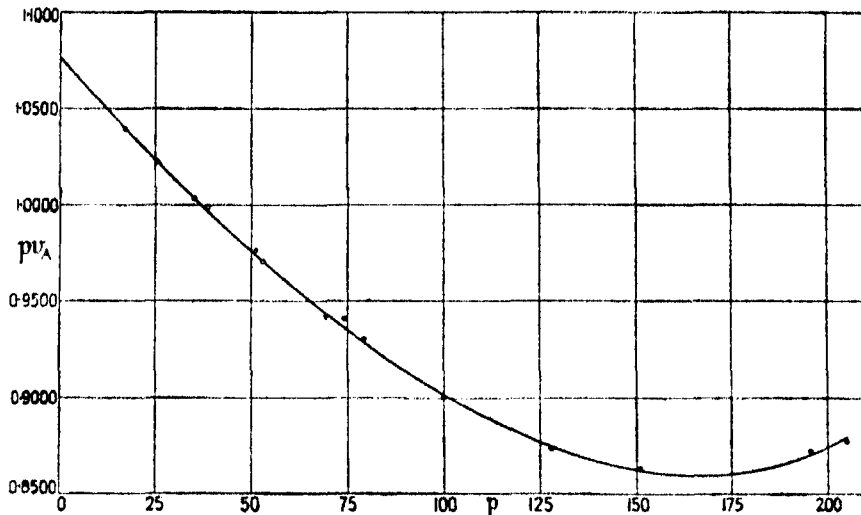


FIG. 2.—Methane Isotherm at 20°C .

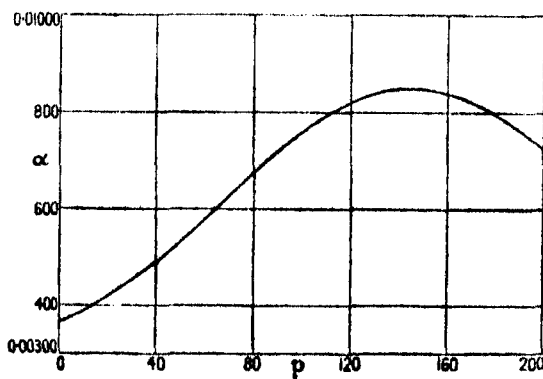


FIG. 3.—Methane; Mean Expansion Coefficient, $0\text{--}20^{\circ}\text{C}$.

of about 125 atmospheres (corresponding to a specific volume of about 8.5), rapidly diverges therefrom at higher pressures and densities; at 165 atmospheres, the deviation is already about 4 per cent., and at 190 atmospheres some 8 per cent. Since the highest pressure employed by K.S.J. was 130 atmospheres, they stopped just short of where the equation begins to fail.

Thirdly, the minimum in the values of pv_A lies at 160–165 atmospheres for the isotherms at 0° and 20°C . This observation receives apparent confirmation from Amagat's data, as quoted in Landolt-Bornstein's tables, which indicate a pv_A -minimum at about 160 atmospheres for an isotherm at 14.7°C .

§ 4. *Triple-point, and Vapour Pressures of Solid Methane.*

Although the connecting tube between the manometer and the bulb containing the liquid or solid phase was about 8 mm. in diameter, it was not found feasible to measure pressures below 0.5 mm. with the present apparatus. During the cooling down of the cryostat to the lowest temperatures, the solid methane always distilled on to the walls of the connecting-tube at the level of the liquid oxygen in the cryostat. As this level gradually falls, the re-distillation to the bulb at the lowest temperatures and pressures is so slow that a false (high) vapour pressure is obtained.

Table III.—Methane : Vapour Pressures of Solid.

Bulb "empty" (E) or "full" (F).	Pressure.	Observed temperature.	Calculated temperature.	Temperature obs. — calc.
	cm.	°	°	°
E	8.767	—182.47	—182.47	0.00
F	8.806	—182.47	—	—
E	3.513	—188.49	—188.48	—0.01
F	3.572	—188.49	—	—
E	1.304	—194.16	—194.13	—0.03
F	1.327	—194.16	—	—
E	0.424	—199.70	—199.68	—0.02
F	0.433	—199.71	—	—
E	0.0506	—208.32	—208.32	0.00
F	0.0495	—208.32	—	—

The experimental results are reproduced in Table III, the expression "empty bulb" indicating that there was only a trace of liquid or solid in the observational bulb, whilst "full bulb" means that about $\frac{1}{2}$ cm.³ was condensed. The small increase in pressure between "empty" and "full" at each temperature shows that there was still some slight impurity in the methane, but, since the corresponding temperature variation is in each case less than 0.1°, the pressures with the "empty" bulb cannot be much in error, and have been used for deriving the following equation :

$$\log p = -517.65/T + 6.7843 - 0.001425 \times T$$

(T = absolute temperature ; p in centimetres.)

Calculated values and their differences from the observed values of the temperature are also given in the table.

The first point in Table III represents the triple-point, for which we have therefore

$$\text{temperature} = 182.47^{\circ} \text{C. ; pressure} = 8.767 \text{ cm.}$$

Crommelin (*loc. cit.*) gives the following values : --

$$\text{temperature} = -183.14^{\circ} \text{C. ; pressure} = 7.0 \text{ cm. ;}$$

but since his observations were based on the rather crude methane used as a cryostat bath, they cannot pretend to much accuracy. As already pointed out, Stock, Henning, and Kuss's measurements (*loc. cit.*) lie outside the range here covered ; the pressure calculated from their equation for the triple-point temperature is 8.721 cm.

Keyes, Taylor, and Smith's (*loc. cit.*) observations also do not extend to the triple-point. A calculation from their equation for the pressure corresponding to a temperature of $-182.47^{\circ} \text{C.}$ gives 8.805 cm., a value which differs from ours by 0.43 per cent., the equivalent temperature difference being only 0.03° .

A very satisfactory confirmation of the triple-point constants as given above was afforded by a similar determination with the second sample of methane, prepared, as stated, in an entirely different manner. The values then found were

$$\text{temperature} = -182.46^{\circ} \text{C. ; pressure} = 8.737 \text{ cm.,}$$

and there was no observable increase in pressure on condensation of about 500 cm.³ of gas. These values are therefore to be preferred to those found for the first sample.

§ 5. *Melting-point Curve.*

With the liquid oxygen cryostat employed, it was not possible to follow the melting-point curve to higher pressures than 46 atmospheres ; the method of determination was based on the melting of a plug of solid methane within a steel capillary tube. Table IV contains, besides the observed temperatures, those calculated from the linear relation

$$t = -182.46 + 2.65 \times 10^{-2} p ;$$

and, although dt/dp is somewhat larger than in the case of carbon monoxide and nitrogen, an extrapolation to the neighbourhood of 200 atmospheres is probably justifiable.

Table IV.—Methane : Melting-point Curve.

Pressure.	Temperature (obs.).	Temperature (calc.).	O — C.
Atms.			
0·115	—182°·46	(Triple-point)	°
16·74	—181·99		+0·03
16·74	—182·00	—182·02	+0·02
31·47	—181·62		0·00
31·45	—181·62	—181·62	0·00
45·85	—181·24		0·00
45·85	—181·26	—181·24	—0·02

§ 6. *Methane-Hydrogen.*

(a) *Three-phase Curve.*—The upper portion of the three-phase curve (the $p-t$ projection of the three-phase strip) was found to have the same form as in the binary systems carbon monoxide-hydrogen and nitrogen-hydrogen, but the point of minimum temperature was barely reached in the range of pressures covered. The experimental results are contained in Table V, and the curve is reproduced in fig. 4.

Table V.—Methane-Hydrogen : Three-phase Curve.

Pressure.	Temperature.	Pressure.	Temperature.
Atms.		Atms.	
0·115	—182°·46	152·08	—184°·12
57·04	—183·34	152·08	—183·97
57·04	—183·46	152·08	—183·97
57·04	—183·46	102·08	—184·02
107·08	—183·84		
107·08	—183·87		

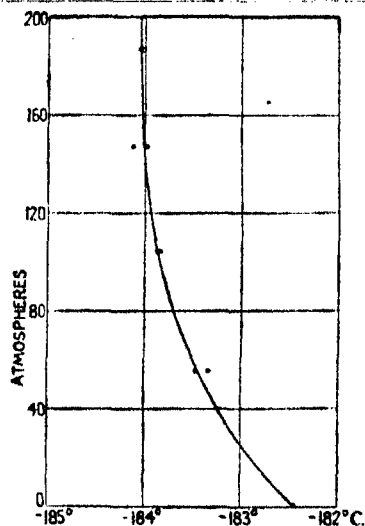


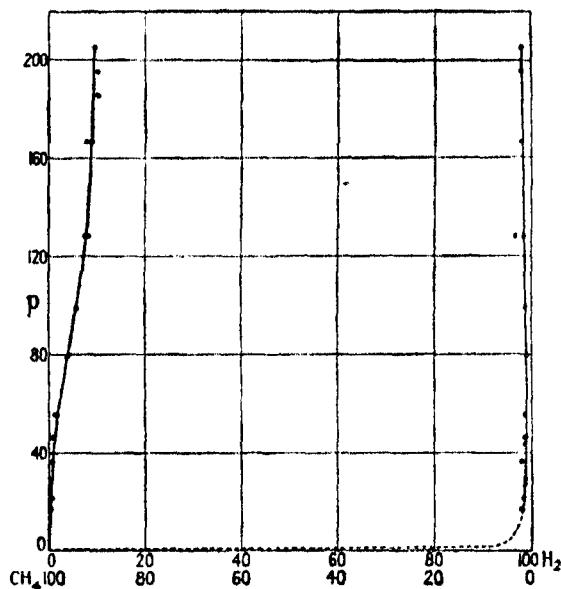
FIG. 4.—Methane-Hydrogen ; Three-phase Curve.

(b) *Isotherm at -182.5° C.*—Since no opportunity presented itself of continuing these investigations in regions of temperature higher than that available to a liquid oxygen cryostat under normal pressures, only one isotherm in the binary system has been determined. The composition of samples of the liquid and vapour phases in equilibrium at various pressures, as found with a Bone and Wheeler gas-analysis apparatus, are given in Table VI, and the isotherm itself is drawn in fig. 5. The concordance between the liquid points is not entirely satisfactory, probably (to a certain extent) because the quantity taken for analysis is of necessity about half the amount taken in the investigation on the other binary systems. It is evident that a definite point of inflection occurs on the liquid branch.

Table VI.—Methane-Hydrogen: *p-x*-Isotherm at -182.5° C.

Temperature	Pressure.	Liquid.		Vapour.	
		H ₂	CH ₄	H ₂	CH ₄
	Atms.	per cent.	per cent.	per cent.	per cent.
-182.53	205.43	9.58	90.42	97.87	2.13
-182.52	205.42	Sample lost		97.60	2.31
-182.48	195.75	10.20	89.80	97.80	2.11
-182.51	186.08	10.16	89.84	No sample	
-182.50	166.78	8.90	91.10	97.83	2.17
-182.54	166.76	7.84	92.16	97.89	2.11
-182.53	128.22	7.60	92.40	96.83	3.17
-182.48	128.19	8.19	91.81	98.46	1.54
-182.52	99.32	5.59	94.41	98.82	1.18
-182.47	79.56	3.83	96.17	99.05	0.95
-182.49	55.82	1.07	98.93	98.85	1.15
-182.49	55.61	1.70	98.30	98.75	1.25
-182.52	46.20	Sample lost		98.95	1.05
-182.50	46.10	0.64	99.36	98.63	1.37
-182.52	43.89	Liquid below outlet		98.95	1.05
-182.50	36.41	0.56	99.44	97.99	2.01
-182.52	29.74	Liquid below outlet		98.57	1.43
-182.48	26.62	Sample lost		98.73	1.27
-182.51	21.61	0.70	99.30	98.54	1.46
-182.47	16.96	Sample lost		97.90	2.10
-182.49	16.89	0.38	99.62	98.35	1.65

On the vapour branch the agreement between individual points is reasonably good. The critical point of contact appears to lie in the neighbourhood of 60 atmospheres, the corresponding proportion of methane in the vapour phase being about 1 per cent.

FIG. 5.—Methane-Hydrogen; p - x -Isotherm at -182.5°C .*Summary.*

§ 1. In recent determinations of the isotherm of methane at 0°C ., the highest pressure employed has been 130 atmospheres and, in view of the probable existence of a pv_{A} -minimum at about 150 atmospheres, the range of pressures is now extended to 215 atmospheres. No satisfactory measurement of the triple-point is available, and there is no modern record of the vapour pressures of the solid phase, or of the melting-point curve. The binary system methane-hydrogen does not appear to have been investigated.

§ 2. The experimental methods here employed will be described in detail in a paper on the ternary system carbon monoxide-nitrogen-hydrogen (to be published shortly). Two different processes were used in the preparation of the methane.

§ 3. Isotherms were measured at 0° and 20°C . up to a pressure of 215 atmospheres. Owing to changes in the resistance-volume factor of the piezometer stem wire, the accuracy did not exceed 1 in 500, but it is evident that a pv_{A} -minimum exists at about 160 atmospheres. Consequently, whilst the present results agree very satisfactorily with those obtained by Keyes and his collaborators, the isotherms for 0°C . derived from their equation of state begins to fail rapidly at pressures above 125 atmospheres, or for specific volumes less than 8.5 cm^3 per gram.

§ 4. Determinations of the triple-point were made with two entirely different samples of methane, and the vapour pressures of the solid were measured down to -208°C .

§ 5. Observations on the melting-point curve extended to $-181\cdot25^{\circ}\text{C}$., the highest temperature attainable with the cryostat.

§ 6. In the binary system methane-hydrogen d^2p/dt^2 was found to be negative along the upper portion of the three-phase curve, as in similar systems. From a $p-x$ isotherm measured at $-182\cdot5^{\circ}\text{C}$. the critical point of contact was found to be in the neighbourhood of 60 atmospheres with a 1 per cent. content of methane in the vapour phase.

Messrs. H. Ryder and J. C. Johnson assisted throughout, both with the experimental work and with the computations. Our thanks are also due to Messrs. M. Jones and E. Hatton, who carried out many of the analyses.

Artificial Disintegration by α -Particles.

By J. CHADWICK, F.R.S., J. E. R. CONSTABLE, B.A., and E. C. POLLARD, B.A.

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§ 1. It is well known that the bombardment of certain elements by α -particles gives rise to the emission of protons, which are ascribed to the disintegration of the nuclei of these elements. It is generally assumed, on the evidence of Blackett's expansion photographs of the artificial disintegration of nitrogen, that the emission of the proton is the result of the capture of the α -particle by the atomic nucleus, which is thereby transformed into a nucleus of the element of the next higher atomic number. We should, therefore, expect to observe certain simple relations between the energy of the incident α -particle and that of the emitted proton, and we should find that the change of energy in transforming a given nucleus is a fixed amount. In certain cases at least the experimental results have led to no such simple relation, and in the case of aluminium Rutherford and Chadwick* have given clear evidence that the energy change in the disintegration is not always the same. The experiments described in this paper were carried out to investigate this question in more detail.

* Rutherford and Chadwick, 'Proc. Camb. Phil. Soc.', vol. 25, p. 186 (1929).

In experiments on artificial disintegration, the emitted protons have usually been detected by the scintillations they produce in a zinc sulphide screen. The scintillation method, though simple and powerful, has certain disadvantages which cannot be avoided. The strain of counting the scintillations is such that the observers must be carefully controlled, and they can be allowed to count only for very limited periods, amounting on the average to about 6 hours per week. The accumulation of results by the scintillation method is thus a long and tedious process. Further, no permanent record of the scintillations can be made.

For these and other reasons it is desirable to use an electrical method of detecting the protons arising from artificial disintegration. The first step in this direction was made by Bothe and Fränz.* They used a Geiger point counter, which, however, has the disadvantage of responding almost equally well to β -particles as to protons or α -particles. Recently Hoffmann and Pose† have been able, by using the very sensitive electrometer devised by Hoffmann, to detect and record photographically the ionisation current produced by a single proton. This method seems not very suitable for general use, for the period of the electrometer is so long that the rate at which particles can be counted is limited to about not more than 1 per minute. Of the electrical methods the most generally applicable are those in which the ionisation current produced by the particle is amplified either by the process of ionisation by collision or by the use of valves. For the experiments described here we have adopted the method of amplification by valves. This method was first successfully employed by Greinacher,‡ and has been further developed by Ortner and Stetter§ and by Ward, Wynn-Williams, and Cave.|| Certain modifications in the designs used by these workers were made for the present application. The general scheme and the method of recording will be described in the next section.

§ 2. *The Detection of Protons.*—The particles to be counted were allowed to enter an ionisation chamber A, the case of which was connected to the positive pole of a battery of about 1000 volts and the inner electrode was connected to the grid of the first valve. The positive ions produced by a particle in the chamber are collected on the inner electrode, and raise the potential of the

* Bothe and Fränz, 'Z. Physik,' vol. 43, p. 456 (1927), and vol. 49, p. 1 (1928).

† Hoffmann and Pose, 'Z. Physik,' vol. 56, p. 405 (1929).

‡ Greinacher, 'Z. Physik,' vol. 36, p. 364 (1926), and vol. 44, p. 319 (1927).

§ Ortner and Stetter, 'Z. Physik,' vol. 54, p. 449 (1929).

|| Ward, Wynn-Williams and Cave, 'Proc. Roy. Soc.,' A, vol. 125, p. 713 (1929).

grid of the valve. This rise of potential is amplified by the first and succeeding four valves. For high sensitivity it is necessary that the initial rise of potential should be as great as possible, *i.e.*, that the first valve should have low inter-electrode capacity and good grid insulation. These conditions were found to be adequately fulfilled by a Marconi D.E.V. valve. The effect of the passage of a particle through the ionisation chamber is to raise the potential of the grid of the first valve by about 10^{-5} to 10^{-4} volts for about 10^{-8} second. The resulting change of anode current causes a variation in the potential drop across an anode resistance, and this is communicated to the grid of the next valve, and so on throughout the amplifier. The connections are shown in the diagram (fig. 1) and involve merely standard amplifier practice. Each stage of

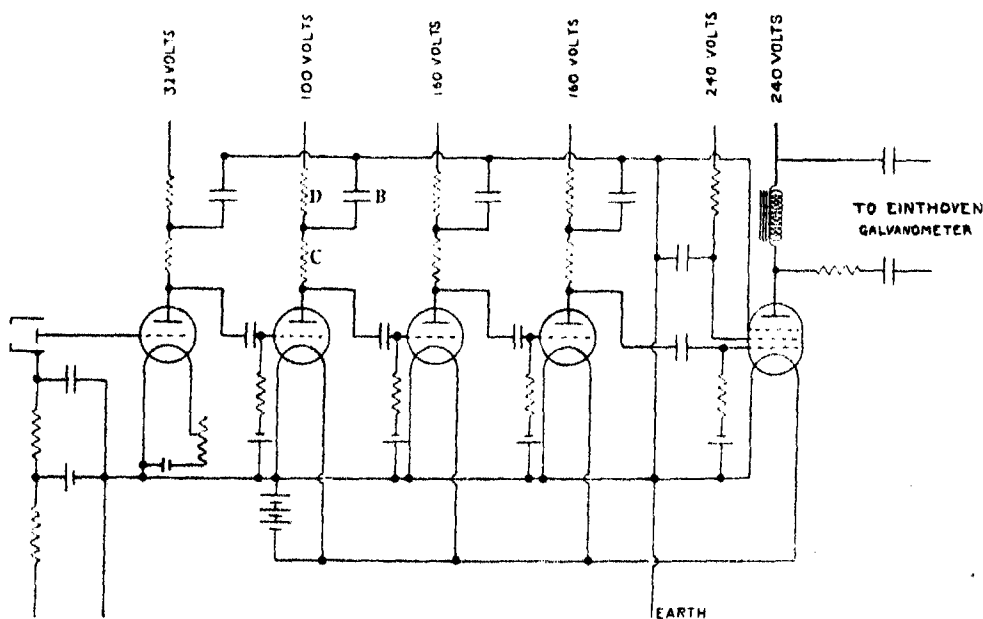


FIG. 1.

amplification was carefully screened from the others by enclosing each valve and its accessories in separate compartments of a metal box. "Feed back" through the high tension batteries was reduced by means of the filter circuits BCD in the battery leads. With the same object separate grid bias batteries were used on each valve. Careful attention to all sources of back coupling was necessary to make the amplifier stable. The second, third and fourth valves were of the Marconi D.E.H. 610 type. For the output valve either a D.E.P. 610 or a P.T. 625 was used.

In order to reduce valve noises the filament temperatures of the first and second valves were kept low, and the anode potentials were reduced to about two-thirds of the normal value. To protect the apparatus from mechanical disturbances each valve was supported in rubber sponges, and the whole amplifier was placed on a firm stone pillar.

As is shown in the diagram, the recording instrument, an Einthoven string galvanometer, was placed in the anode circuit of the last valve. The steady component of the anode current was prevented from passing through the galvanometer by a choke-capacity filter circuit. A variable shunt was connected across the galvanometer to allow adjustment of the sensitivity. The deflections of the string were recorded photographically on a strip of moving bromide paper. The camera used was the standard pattern of the Cambridge Instrument Company. The cylindrical condensing lens of the camera has engraved upon it a millimetre scale, which is reproduced in the photographic record. It is thus a very simple matter to measure the size of the deflections of the galvanometer, when such a procedure is required. A typical record of the deflections due to the entry of disintegration protons into the ionisation chamber is shown in fig. 2. The kicks are not all of the same size, for the protons



FIG. 2.

entering the chamber differed in speed. The ionisation per centimetre path produced by a proton will depend on the speed in much the same way as that due to the α -particle. Thus a fast proton will cause a much smaller deflection of the galvanometer than one which is near the end of its range when it enters the ionisation chamber. In certain cases valuable information can be deduced from a comparison of the sizes of the deflections. It was to facilitate such a comparison that an ionisation chamber of the parallel plate type, shown in fig. 3, was used in these experiments. While this has a relatively high electrode

capacity, thus reducing the rise of potential on the first grid, it has the advantage that the paths of particles which enter the chamber at different angles are practically equal and that the time of collection of the ions is the same for different paths. Thus particles of the same velocity should produce nearly equal deflections of the galvanometer.

In preliminary investigations and in cases where no permanent record of the protons was required, the string galvanometer was replaced by telephones. The output from the last valve was sufficient to work several sets of telephones in parallel, so that two or more observers could count simultaneously. The clicks produced by protons were as a rule easily audible; difficulty was only experienced with protons of extremely high speed.

§ 3. *Experimental Procedure and Results.*

The experiments consisted in bombarding a target of an element by the α -particles from a polonium source, and observing the disintegration protons either in the direction of the incident α -particles or at right angles to it. Absorption curves of the protons were obtained by placing sheets of mica of known thickness in their path to the ionisation chamber, and counting the number of protons at each absorption.

The source of α -particles was a platinum disc of 3.5 mm. diameter, coated with polonium. The polonium was obtained on a platinum foil by the electrolysis of a solution of radium ($D + E + F$), and was concentrated on the platinum disc by volatilisation in a current of hydrogen. The amount of polonium was about 5 millicuries at the beginning of the experiments.

The arrangement used for observation in the forward direction is shown in fig. 3. The material under examination—either in the form of a thin foil or as a thin layer of powder dusted on to a gold foil—was placed from 1 to 2 mm. in front of the polonium source S. The gold foil served also to close the tube T.

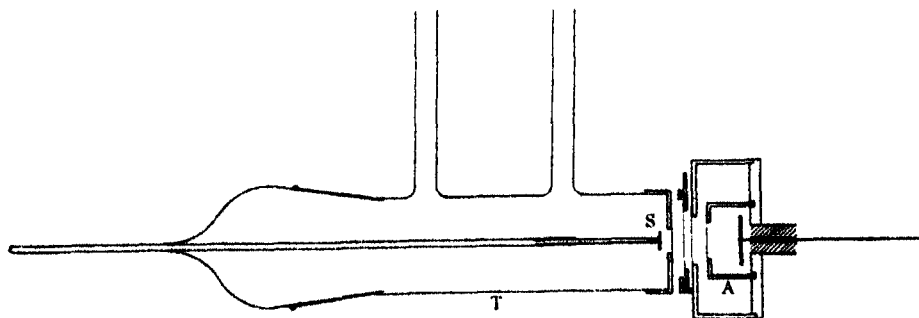


FIG. 3.

Oxygen was passed through the tube T, containing the source and bombarded material, to avoid disintegration protons from the nitrogen of the air. The ionisation chamber A was connected to the positive pole of a battery of 1000 volts. The collecting electrode was insulated by quartz, and was connected to the grid of the first valve through an earthed guard tube. In order to protect the insulated system from electrical disturbances the ionisation chamber was enclosed in an earthed case. Absorbing screens of mica could be inserted in a holder, placed between the tube T and the ionisation chamber.

For the observations of the protons emitted at right angles to the direction of the incident α -particles the arrangement shown in fig. 4 was used. The source

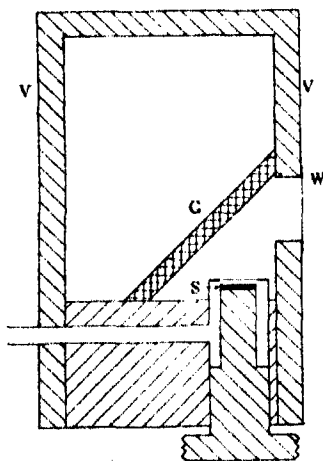


FIG. 4.

S was enclosed in a small tube, carried in the brass box V, V. The material to be bombarded was placed on the graphite sheet G. The disintegration protons passed through the window W into the ionisation chamber. The brass box and the tube containing the source were evacuated separately in order to avoid contamination of the box by aggregate recoil from the source. The face of the source tube was closed by a sheet of mica of approximately 1 mm. air equivalent. The window W through which the protons were observed was closed by a silver foil of 3.8 cm. air equivalent.

With these experimental arrangements, several elements were examined for disintegration. Absorption curves for the disintegration protons were plotted by counting the number of protons entering the ionisation chamber per minute when sheets of mica of various air equivalents were placed in the path of the protons. The following elements were examined: lithium, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus and sulphur. Disintegration protons were observed with certainty from boron, nitrogen, fluorine, sodium, aluminium and phosphorus. For the others no definite effect was found under the conditions of our experiments. It must be noted, however, that the experiments were not pursued down to small absorptions; an emission of protons of short range would therefore not be detected. In the experiments in the forward direction the experiments were limited by the presence of "natural" protons, due to hydrogen in the source of polonium and in the materials exposed to the α -particles. These

have a maximum range of about 16 cm. in air, under our experimental conditions. The observations at right angles were taken to an absorption corresponding to about 7 cm. of air.

In nearly all cases the thickness of the material exposed to the bombardment of the α -particles was sufficient to absorb the α -particles completely. Further, as will be seen from figs. 3 and 4, the geometrical conditions are such that neither the pencil of α -rays incident on the radiator, nor the pencil of protons received by the ionisation chamber is well defined. This is more especially the case in the experiments carried out in the forward direction. The protons observed under these conditions are thus due to α -particles of all velocities from zero up to a certain maximum (slightly less than the initial velocity of polonium α -particles owing to the absorption in the path to the radiator) and comprise particles which are emitted over a wide range of angles with respect to the direction of the disintegrating α -particle. Moreover, the divergence of the beam of protons entering the ionisation chamber is such that the paths in the absorbing screens differ markedly. The conditions of experiment are thus far from ideal, and we cannot expect the results to show singularities, such as the presence of groups of protons, as clearly as under conditions more precisely defined. These circumstances must be taken into account when judging the experimental results given below.

Boron.—The element boron was examined in the form of a layer of powdered amorphous boron (Kahlbaum) and of powdered boron trioxide. Some of the results obtained are shown in fig. 5. Both curves refer to protons observed in a direction at right angles to the incident α -particles; for the upper curve the maximum range of the α -particle was about 3.8 cm., and for the lower about 2.8 cm. It will be seen that there are two groups of protons emitted in the disintegration of boron. The existence of the group of 20 cm. range was confirmed by an examination of the sizes of the kicks on the records. As the absorption in the path of the protons was increased the fraction of large kicks grew until an absorption of about 18 cm. was reached, when it fell very rapidly. This indicated that a group of slow protons ended in this region. The variation in the average size of the kicks with the absorption in the path of the protons is shown in fig. 6. These two groups were also found in the experiments in the forward direction. With α -particles of 3.8 cm. maximum range incident on the boron radiator the ranges of the groups were approximately 32 cm. and 76 cm. observed in the forward direction. In addition, a third group of range about 16 cm. was found but, on account of the large number of natural protons emitted by our polonium source, it was difficult to decide whether any

part of this group could be ascribed with certainty to boron. Good evidence that a third group is present in the disintegration protons from boron is,

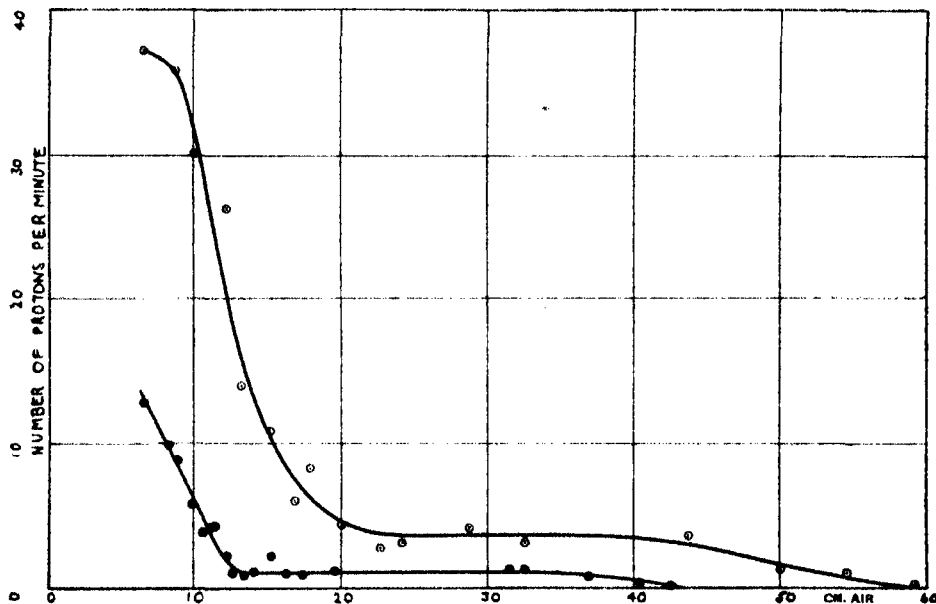


FIG. 5.—Absorption Curve for Protons from Boron.

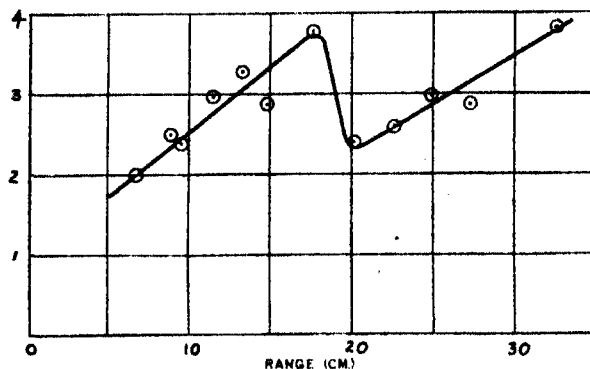


FIG. 6.—Average size of kicks.

however, afforded by the experiments of Bothe and Fränz,* and later of Bothe.†

Nitrogen.—Nitrogen was examined both as gas and in the form of a layer of paracyanogen. The results obtained in the experiments in the forward

* Bothe and Fränz, 'Z. Physik,' vol. 49, p. 1 (1928).

† Bothe, 'Z. Physik,' vol. 63, p. 381 (1930).

direction are shown in fig. 7. The α -particles, of maximum range 3.9 cm., had a path of about 3 mm. in nitrogen. Here, also, difficulty was experienced

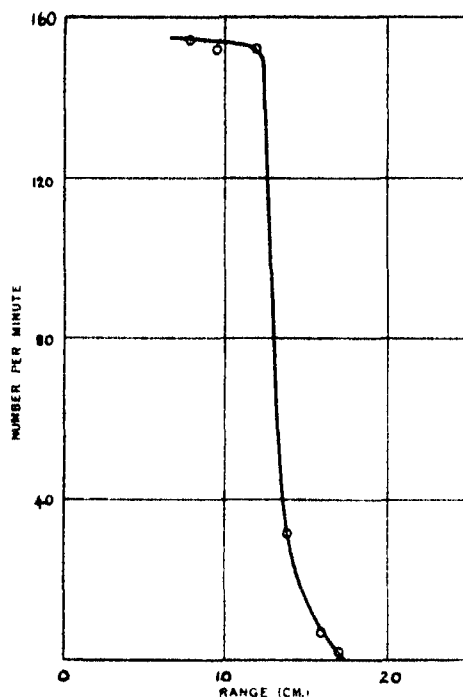


FIG. 7.—Absorption Curve for Protons from Nitrogen.

in allowing for the effect of the natural protons and the measurements at absorptions less than 10 cm. of air are approximate only. The curve suggests that the protons for nitrogen consist of a definite group of maximum range about 17.5 cm.

Fluorine.—A layer of finely-powdered calcium fluoride, CaF_2 , served for the experiments with fluorine. The absorption curves for the protons liberated by α -particles of maximum range 3.8 cm. are shown in fig. 8, the upper curve for the forward direction, the lower for the right angle direction. The protons appear to be heterogeneous and there is no suggestion of distinct groups. Some experiments by the right angle method in which incident α -particles of shorter range were used indicated a flattening of the absorption curve at small absorptions, but there was still a greater degree of heterogeneity than could be explained by the effect of the experimental conditions.*

* [Note added in proof.—Later experiments show that the protons emitted from fluorine consist of at least three distinct groups.]

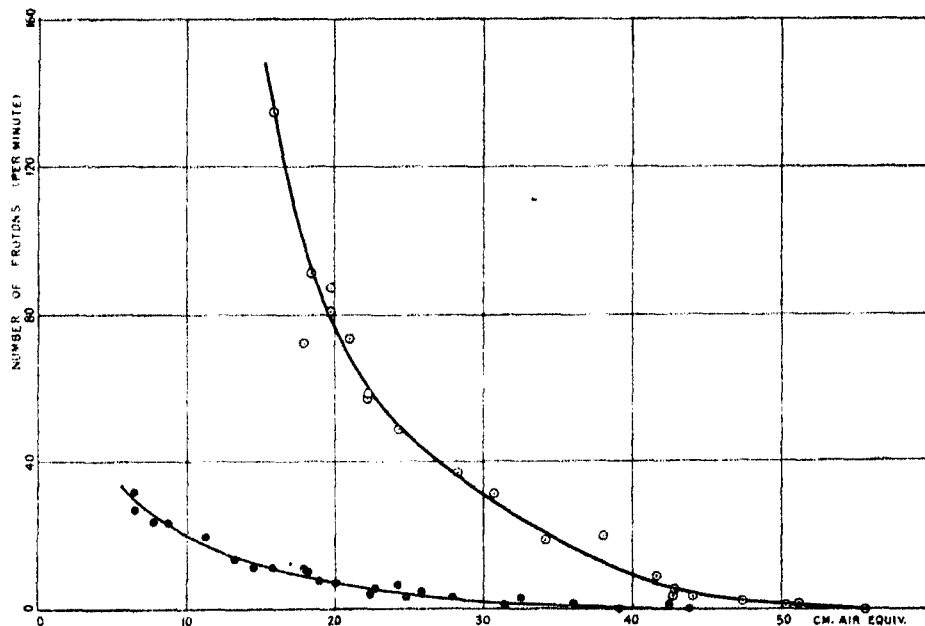


FIG. 8.—Absorption Curve for Protons from Fluorine.

Sodium.—The absorption curve obtained for sodium, examined as a thin layer of NaOH, was similar to that shown above for fluorine, and suggested a heterogeneous distribution of protons rather than one or two discrete groups. The maximum range of the proton observed in the forward direction was about 44 cm. for incident α -particles of 3.8 cm. maximum range.

Aluminium.—The absorption curves for the protons liberated in the forward direction from aluminium (a foil of 4 cm. stopping power) are shown in fig. 9. In general, the results are similar to those obtained with boron. Considering first the upper curve, obtained with incident α -particles of 3.7 cm. maximum range, we conclude that there are two main groups of protons with ranges about 32 cm. and 65 cm. The third prominent group, of range about 15 cm., may be due entirely to the natural protons from the source. There is, further, a weakly-marked group of range about 52 cm. Owing to the well-known probability fluctuations it is difficult to be certain of such small changes in the numbers of observed particles as the separation of this group depends on. For each point in the neighbourhood of this range about 500 particles were counted, and the evidence from the numbers was confirmed by an examination of the sizes of the deflections due to the particles. We may infer that this group is real; as we shall see later, Pose has obtained very definite evidence on this point.

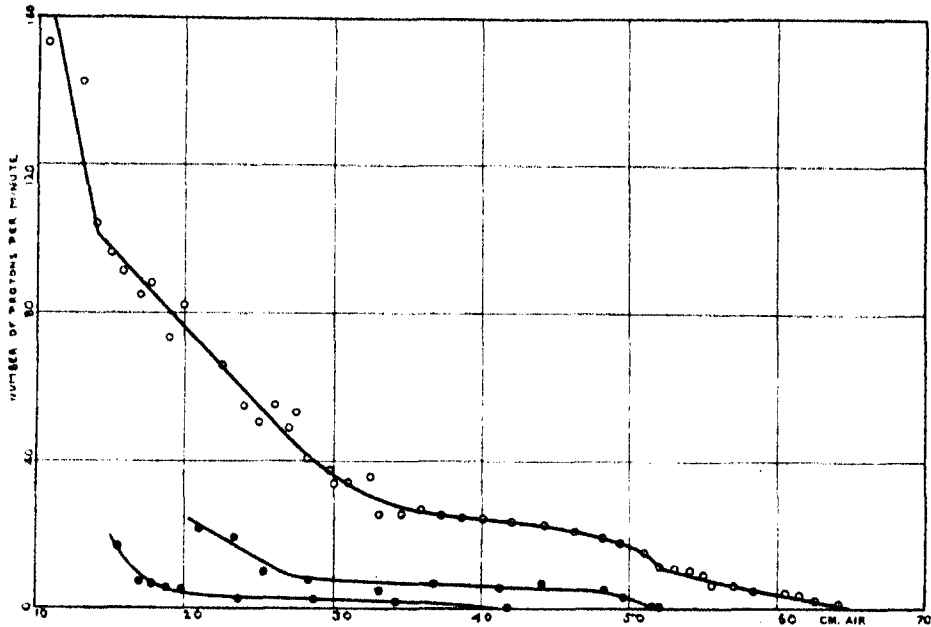


FIG. 9.—Absorption Curve for Protons from Aluminium.

The curve obtained with α -particles of 3.15 cm. maximum range shows two groups of ranges, 27 cm. and 52 cm., and with α -particles of 2.9 cm. maximum range two groups with ranges about 17 cm. and about 42 cm. In the latter case the number of particles was very small and the ranges of the groups could not be determined with any accuracy. Experiments by the right angle method showed the presence of two groups corresponding to the two main groups observed in the forward direction. The ranges of these groups were 21 cm. and 51 cm. for incident α -particles of 3.8 cm. maximum range.

Phosphorus.—Phosphorus was used in the form of a layer of powdered red phosphorus. The absorption curve of the protons observed at right angles with incident α -particles of 3.8 cm. maximum range is shown in fig. 10. It consists of a single group of protons. Experiments in the forward direction

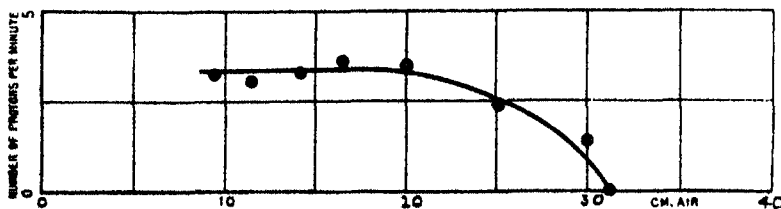


FIG. 10.—Absorption Curve for Protons from Phosphorus.

confirmed this result, but were not so definite owing to the poorer geometrical conditions.

§ 4. *Discussion of Artificial Disintegration.*

It has been generally assumed, largely on the basis of Blackett's photographs of the disintegration of the nitrogen nucleus, that the process of artificial disintegration of an atomic nucleus by collision of an α -particle is due to the penetration of the α -particle into the nucleus. The α -particle is absorbed into the nuclear system and a proton is emitted. The energy relations in the disintegration process should therefore be very simple. Assuming that momentum is conserved in the collisions, it should be possible to draw a definite conclusion about the energy change from the original to the final nucleus by measuring the energies of the protons released by α -particles of known energies. From such experiments on the disintegration of aluminium Rutherford and Chadwick (*loc. cit.*) concluded that the change of energy from the original nucleus (aluminium) to the final nucleus (silicon) was not always the same. They suggested that perhaps all nuclei of the same type were not identical but could have masses or energies differing by small amounts. This would be the case if the energy levels of the proton in α -particles in the nucleus were not well defined. Such a supposition is, however, difficult to reconcile with the modern views of nuclear structure.

The experiments described in the previous section (and those of Bothe, Fränzl, and Pose, which appeared while this account was in course of preparation) suggest the presence of distinct groups in the protons released in disintegration, and they permit us to give a more definite picture of the process of artificial disintegration, and one which will interpret the experimental results in terms of the detailed structure of the nucleus.*

Consider a nucleus with a potential field of the type shown in fig. 11. The potential barrier for the α -particle is given by the full line, that for the proton, since it has only half the charge of the α -particle, by the dotted line. Suppose that a proton exists in the nucleus in a stable level $-E_p^0$. Assuming first that the α -particle is captured in the disintegration process, let the level in which the α -particle remains after capture be $-E_\alpha^0$. If an α -particle of kinetic energy E_α penetrates into this nucleus and is captured, the energy of the proton emitted in the disintegration will be $E_p = E_\alpha + E_\alpha^0 - E_p^0$, neglecting the small kinetic energy of the residual nucleus. There may, of course, be more than one proton level in the nucleus, or there may be more than one level

* Chadwick and Gamow, 'Nature,' July 12, 1930.

in which the α -particle may be captured. There will then be correspondingly more groups of disintegration protons. This type of disintegration, by

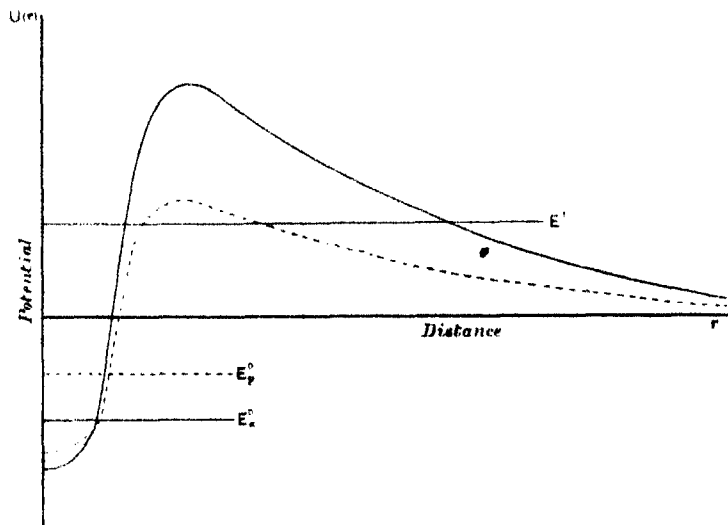


FIG. 11.

capture of the α -particle, will always give rise to a group of protons of definite energy, and the energy spectrum of the disintegration protons will consist of a number of lines, each of which is defined by one proton and one α -level. The kinetic energy of the proton group will be greater or less than that of the incident α -particles according as E_p^0 is greater or less than E_α^0 , that is, according as the α -level is deeper or higher than the proton level.

It seems possible on general grounds that disintegration may occur in another way, by the ejection of a proton without capture of the α -particle. The α -particle may cross the potential barrier and be re-ejected, but it seems likely that this process of disintegration would generally occur without penetration into the nuclear system. If the nucleus disintegrates without capture, the initial kinetic energy of the α -particle will be distributed between the emitted proton and the escaping α -particle (again neglecting the recoiling nucleus). In this case the disintegration protons may have any energy between $E_p = 0$ and $E_p = E_\alpha - E_p^0$.^{*} The energy spectrum of the protons will be a continuous distribution with a maximum energy less than that of the incident α -particle, and less than that of the line spectrum arising from the same proton level by capture of the α -particle. If the disintegrating nucleus has two or

^{*} It is assumed that no change occurs in the level system of the nucleus.

more occupied proton levels there will be two or more continuous spectra, provided that the energy of the incident α -particles is sufficiently great. If both types of disintegration occur, the energy spectrum of the ejected protons will, for the simplest type of nucleus with one proton and one α -level, be divisible into two parts, a continuous spectrum and a line (cf. fig. 12). The

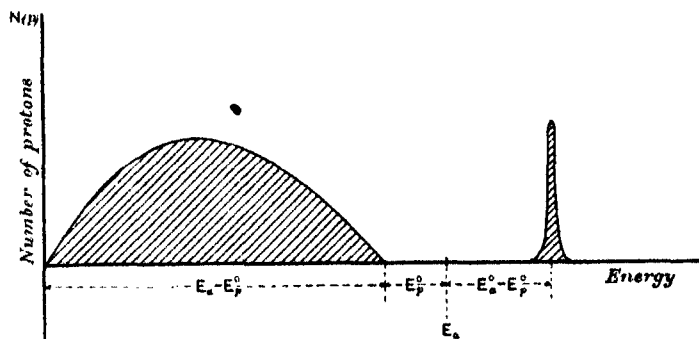


FIG. 12.

energy of the line group may be greater or less than the energy of the original α -particles, but it will always be greater than the upper limit of the continuous spectrum.

The accurate measurement of the upper limit of the continuous spectrum and of the line will allow us to estimate the values of the energy levels of the proton and α -particle in the nucleus.

In actual experiment the separation and arrangement of the groups of protons may not be so simple as we have made it appear. The numbers of disintegration protons to be observed are so small that definite conditions of disintegration cannot be attained experimentally. The initial beam of α -particles may be homogeneous, but, since thick layers of bombarded material must generally be used to obtain sufficient effect, the protons observed arise from disintegrations due to α -particles of widely different energies. For the same reason, both the pencil of α -particles and that of the ejected protons must be of wide angle; this confuses the results since the energy of the ejected proton will depend on its direction relative to that of the α -particle responsible for it.

In distinguishing between a continuous spectrum and a line spectrum, the distribution of the protons with angle may be of importance. It is to be expected that the protons of a line spectrum, resulting from capture of the α -particle, will be emitted nearly uniformly in all directions. On the other

hand, the continuous spectrum probably arises chiefly from collisions in which the α -particle does not penetrate the nucleus. These protons may not be emitted uniformly in all directions but perhaps mainly in the forward direction.* Thus observations of the intensity of a proton group in the same direction as the incident α -particle and at right angles may help to decide whether the group belongs to the continuous or line type.

A further point which may be mentioned here is the possibility of the occurrence of line spectra due to a resonance between the incident α -particle and the nucleus. This possibility was first clearly pointed out by Gurney.† Suppose that the nucleus has a possible, but unstable, α -particle level E' (see fig. 11). If the incident α -particles have exactly energy E' their chance of penetrating the barrier will be unity and much larger than the chance for particles of greater or smaller energy. Thus if a thick layer of material is bombarded by α -particles of initial energy greater than E' there will appear a line group of protons corresponding to the increased chance of capture of α -particles of energy E' . Evidence for resonance lines of this type appears in the results obtained with aluminium (fig. 9), but it is shown much more definitely in some experiments of Pose which were published while this account was in course of preparation. This point will be raised again later.

We shall now proceed to the interpretation of our experimental results. The experiments give the ranges of the protons released under certain conditions by α -particles of known initial energy. The ranges of the protons are actually measured mainly in mica and expressed in equivalent centimetres of air on the assumption that a thickness of mica of weight 1.43 mg. per square centimetre is equivalent in stopping power to 1 cm. of air at 15° C. and 760 mm. From these ranges we have to deduce the energies of the protons. For α -particles of lower velocity than the protons concerned in these experiments the range varies as the cube of the velocity; for β -particles of higher velocity than our protons the range varies as the fourth power of the velocity. In the absence of definite information, we shall assume that for the protons with which we are dealing the range varies as (velocity)^{3.5}. Knowing that a proton of velocity 3.08×10^9 cm. per second (the proton propelled by a direct collision of an α -particle of velocity 1.922×10^9 cm. per second) has a range of 32 cm. measured in the above way, we can calculate with sufficient accuracy for the present purpose the energies of protons of different ranges.

* See, however, Beck, 'Z. Physik,' vol. 65, p. 22 (1930).

† Gurney, 'Nature,' vol. 123, p. 565 (1929).

If the α -particle is captured by the nucleus then the conservation of momentum in the collision gives

$$MV = m_p v_p \cos \psi + m_n v_n \cos \omega$$

$$0 = m_p v_p \sin \psi - m_n v_n \sin \omega,$$

where M, V ; m_p, v_p ; and m_n, v_n are the masses and velocities of the α -particle, proton and residual nucleus respectively, and ψ, ω are the angles between the incident track of the α -particle and the directions of motion of the proton and nucleus respectively.

If the disintegration of the nucleus takes place with a release of energy Q , we shall have

$$\frac{1}{2}m_p v_p^2 + \frac{1}{2}m_n v_n^2 = \frac{1}{2}MV^2 + Q.$$

The experimental results give the maximum range of the proton emitted under the specified conditions. In the experiments in the forward direction this maximum range will correspond to $\psi = 0$. In the experiments in which the protons were observed at right angles to the α -particle beam the maximum ranges will correspond to the smallest value of ψ possible under the conditions. For the accuracy attained at present, however, it will be sufficient to assume that these ranges observed at right angles actually correspond to $\psi = 90^\circ$. We then find, for the experiments in the forward direction,

$$Q = \{m_p v_p^2 (m_p + m_n) - MV^2 (m_n - M) - 2MV \cdot m_p v_p\} / 2m_n$$

and for the experiments at right angles

$$Q = \{m_p v_p^2 (m_p + m_n) - MV^2 (m_n - M)\} / 2m_n,$$

where v_p is the maximum velocity of the proton observed in the specified conditions.

If the nucleus disintegrates without capture of the α -particle a term must be added to the above momentum and energy relations to express the motion of the α -particle after the collision. Calculation shows, however, that the maximum value of v_p occurs when the α -particle and nucleus move with the same velocity and in the same direction after the collision. The above expressions for Q are thus valid for the continuous as well as for the line spectra, and m_n will have the same numerical value in both cases, although a different meaning.

In the case of capture of the α -particle $Q = E^\circ_p - E^\circ_\alpha$ and in the case of non-capture, $Q = E^\circ_p$.

§ 5. Examination of Experimental Results.

We shall consider first the results with boron. Taking first the experiments in the forward direction, groups of protons with ranges 32 cm. and 76 cm. were found when the incident α -particles were of 3.8 cm. range. Both these groups were found in the direction at right angles, with ranges 20 cm. and 57 cm. for α -particles of 3.8 cm., and ranges 13 and 40 cm. for α -particles of 2.8 cm. range. The energy changes Q calculated from these figures are, for the group of shorter range, $+0.1$, $+0.3$, $+0.26$, $\times 10^6$ electron volts, an average of $+0.2 \times 10^6$ electron volts; for the longer group, $+3.0$, $+3.5$, $+3.2 \times 10^6$, an average of 3.2×10^6 electron volts.

There can be no doubt that the latter is a line group corresponding to the capture of the α -particle in the disintegration process. The identification of the shorter group is not so clear; the energy change is positive but, owing to error in the estimation of the range of the protons and to further uncertainty in the deduction of their energy, this evidence is not very definite. It is, however, supported to some extent by the shape of the absorption curve as obtained here and also in the experiments of Bothe and Fränz. We shall assume that this group also is the result of capture of the α -particle.

There is thus no evidence in our experiments for the process of ejection of the proton without capture of the α -particle, and for this we must turn to the experiments of Bothe and Fränz, confirmed later by Bothe.* These workers found in the proton emission of boron bombarded by polonium α -particles a heterogeneous group with a maximum range of about 16 cm. It is difficult to be quite certain that this group does not arise from hydrogen impurity in the boron, but in both sets of experiments great care was taken to eliminate this source of error. Assuming that this group arises from boron we find an energy change of -1.4×10^6 e-volts in this disintegration. It is worthy of note that Bothe's experiments show that this group has a very different angular distribution from the other (line) groups; it is emitted mainly in the forward direction.

We have now to consider the disintegration process from another point of view and to make use of the measurements of the masses of nuclei. If the mass of the nucleus before disintegration is known, then the mass of the nucleus formed in the disintegration can be deduced at once from the observed energy change. It is, however, simpler to deal with the mass defects of the nuclei rather than with their masses.† The mass defect is the difference between

* *Loc. cit.*, p. 470.

† Cf. Gamow, 'Proc. Roy. Soc.,' A, vol. 126, p. 632 (1930).

the sum of the masses of the constituent particles of the nucleus when free and their mass combined as a nucleus, and therefore represents the energy which has been released in the formation of the nucleus or the energy of binding of the particles. In this calculation it is assumed that a nucleus consists of α -particles, protons, and electrons, and that the number of α -particles is as large as possible. Thus we assume that the boron isotope B_{11} consists of two α -particles, three protons, and two electrons. The mass of the B_{11} nucleus deduced from Aston's measurement of the mass of the atom is 11.0083 ± 0.0016 , and its mass defect is $(16.7 \pm 1.6) \times 10^{-3}$ mass units. The mass unit is defined on Aston's basis of $O_{16} = 16$. An energy of 1 million electron volts corresponds to a mass of 1.07×10^{-3} on this scale, so that the total (negative) energy of the particles comprising the B_{11} nucleus is nearly 16×10^6 e-volts. In fig. 13 the mass defects of the lighter elements are plotted against the number, n , of α -particles in the nucleus, the values taken from Aston's data* being marked with a cross. We are here concerned with the energy changes when a proton is emitted from a nucleus either with or without capture of an α -particle, that is, with the change in mass defect as one nucleus is transformed into the next, either of higher or lower atomic number. The errors in the mass defects, as deduced from Aston's measurements, are about 2×10^{-3} mass units for the lighter elements. They are thus of the same magnitude as the energy changes observed in the disintegrations. These errors are, however, the maximum which can be allowed in the measurements, and the probable error may be taken as about one-third of those given by Aston.

We return now to the disintegration of boron. It is natural to ascribe the observed phenomena to the disintegration of the isotope B_{11} , for this is present in the proportion of about 4 parts to 1 part of B_{10} . The nucleus formed from B_{11} with capture of the α -particle will be a carbon isotope of mass 14. In the process in which there is observed a release of energy of 3.2×10^6 e-volts there will be formed a C_{14} nucleus with a mass defect of $(16.7 + 3.3 = 20 \pm 1.6) \times 10^{-3}$ mass units. Now the mass defect of N_{14} is $14 \pm 2.8 \times 10^{-3}$, and this nucleus differs from C_{14} only by the absence of one electron. According to a calculation of G. Gamow, a K electron of N_{14} penetrates into the nucleus about 10^{20} times per second. If the mass defect of C_{14} were greater than that of N_{14} the change $N_{14} \rightarrow C_{14}$ could take place with a release of energy, and it would be difficult to understand why N_{14} is abundant and C_{14} is unknown. We must conclude that the mass defect of C_{14} is less than that of N_{14} , and therefore that this disintegration cannot be due to the isotope B_{11} .

* Aston, 'Proc. Roy. Soc.,' A, vol. 115, p. 487 (1927).

The other capture disintegration with a release of energy of 0.2×10^6 ϵ -volts leads to a C_{14} nucleus of mass defect $(16.9 \pm 1.6) \times 10^{-3}$. Comparing this with the mass defect of N_{14} $(14.0 \pm 2.8) \times 10^{-3}$, and remembering that the probable errors in the defects are about one-third of those given, we see that it is not impossible but nevertheless unlikely that the disintegration can be ascribed to B_{11} .

In a similar way it can be shown that the disintegration without capture cannot be ascribed to the transformation $B_{11} \rightarrow Be_{10}$, for this Be_{10} nucleus would have a mass defect $(15.3 \pm 1.6) \times 10^{-3}$ while that of B_{10} is $(6.5 \pm 1.5) \times 10^{-3}$.

We shall therefore assume that the disintegration phenomena observed for boron must all be attributed to the isotope B_{10} . Unless the capture process with small change of energy is really due to B_{11} , it seems that, if B_{11} can be disintegrated, the emitted protons have not been separated in our observations from those emitted by B_{10} . The nuclei formed by the disintegration of B_{10} will be Be_9 , without capture of the α -particle, and C_{13} with capture. Since we observe two types of capture, it follows that two types of C_{13} nucleus can be formed. We must suppose that the disintegration accompanied by the energy change of 0.2×10^6 ϵ -volts gives rise to an excited C_{13} nucleus which must change very shortly into the stable nucleus* corresponding to the disintegration with an energy change of 3.2×10^6 ϵ -volts. The energy released in this change will be emitted as a γ -radiation of $h\nu = 3 \times 10^6$ ϵ -volts. It is of interest to note that Bothe and Becker† have recently reported the emission of a radiation of about this energy when boron is bombarded by polonium α -particles.

In the disintegration without capture there is an energy change of -1.4×10^6 ϵ -volts. If there is no change in the level system of the nucleus in the disintegration, we can conclude that the proton level of the B_{10} nucleus is at -1.4×10^6 ϵ -volts. We assume that both protons are in this level. The total energy defect of the B_{10} nucleus is about 6×10^6 ϵ -volts. We shall ascribe the difference between the total defect and the defect of the protons to the two α -particles, for nothing definite can yet be said about the behaviour of electrons in a nucleus. The α -particles of the B_{10} nucleus will then be at a

* [Note added in proof.—The mass defect of C_{13} deduced from these experiments is $(9.9 \pm 1.7) \times 10^{-3}$. King and Birge ('Astrophys. J.', vol. 72, p. 19 (1930)) have recently obtained, from the band spectrum of carbon, a comparison of the masses of C_{12} and C_{13} which leads to a value $(11 \pm 2) \times 10^{-3}$ for the mass defect of C_{13} .]

† Bothe and Becker, 'Naturwiss.', vol. 31, p. 705 (1930).

level of about -1.6×10^6 e-volts. We may suppose that the capture disintegrations of boron occur in the following way. The α -particle is captured into the stable α -particle level of the B_{10} nucleus. One type of disintegration corresponds to the immediate emission of a proton, before there is any general change in the level system, with a release of energy of 0.2×10^6 e-volts. The second type is obtained when a reorganisation of the nucleus takes place before the emission of the proton, and an extra amount of energy is released. This picture of the B_{10} nucleus and its disintegration processes is consistent with the available data, but it must be admitted that it is speculative and the processes may not be so simple as we have supposed.

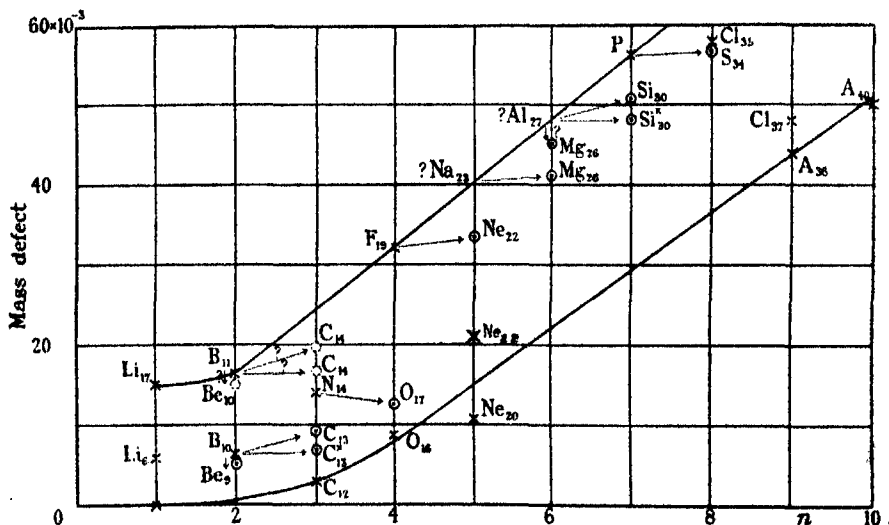


FIG. 13.—The mass defects are plotted against the number, n , of α -particles assumed to exist in the nucleus. The unit of ordinates is 10^{-3} mass units ($O_{16} = 16$), and is equivalent to 0.93×10^6 e-volts. The mass defects deduced from Aston's data are denoted by $\times$, those from disintegration experiments by $\odot$.

Nitrogen.—In the case of nitrogen we have evidence of one group of protons, corresponding to a capture of the α -particle. The energy change Q is about -1.3×10^6 e-volts. The scintillation experiments of Rutherford and Chadwick, in which the incident α -particles had a range of 7 cm., lead to an energy change of about -1.4×10^6 e-volts; the agreement is very satisfactory. We conclude that in nitrogen the level of the protons is much deeper than the α -particle level. The nucleus formed in the disintegration of nitrogen is O_{17} . Its mass defect deduced from these experiments is given in fig. 13.

It may be noted that Blackett observed seven disintegrations of nitrogen

in which the α -particle was captured and none without capture. It seems probable that disintegration of nitrogen without capture occurs relatively seldom. The result of such a disintegration is the formation of a C_{13} nucleus. The mass defect of this nucleus has been obtained from the boron experiments, and it appears that the transformation $N_{14} \rightarrow C_{13}$ requires an expenditure of energy of about 3.9×10^6 e-volts. We are thus able to account in a general way for the difficulty of this type of disintegration.

The combination of both results leads to a picture of the nitrogen nucleus in which the three α -particles are on a level of about -2 to -2.5×10^6 e-volts, and the two protons at a lower level, about -3.5 to -4×10^6 e-volts, a scheme which is in fair agreement with the known mass defect of the nitrogen nucleus.

Aluminium.—In discussing the evidence on the disintegration of aluminium it is convenient to consider first the origin of the weak group of range 52 cm. It has been suggested above that this group is the result of a resonance between α -particles of a certain definite velocity and a “false” level in the aluminium nucleus. The evidence for this explanation depends mainly on the experiments of Pose.* Pose found in fact that the proton group of long range consists of two parts, one group of range 50 cm. and another of range 60 cm.† He was able to show that the 50 cm. group occurs only when α -particles of 2.56 cm. range are present in the bombarding beam of particles, and that the 60 cm. group is due only to α -particles of 3.51 cm. range. Both groups are therefore due to resonance of the type suggested by Gurney which was mentioned in the previous section. The energies of the resonance levels deduced from these results are about 3.9×10^6 e-volts and 4.8×10^6 e-volts.

According to Pose these two resonance groups account for the whole of the protons of long range. Such a result would mean that penetration of the potential barrier of the aluminium nucleus is only effected when resonance occurs, that α -particles which have not the energy corresponding to a “false” level have no chance, or at most an exceedingly small one, of penetrating into the nucleus. Our experiments, on the other hand, suggest that α -particles which are not in resonance with the nucleus are nevertheless able to cause a detectable amount of disintegration, but in our opinion neither our own results nor those of Pose are sufficient to give a decisive answer on this question.

Until this point is decided the results of experiments on the disintegration of

* Pose, ‘Z. Physik,’ vol. 64, p. 1 (1930).

† Pose gives the ranges at 0° C. and 760 mm. We give here the ranges at 15° C. and 760 mm. in accordance with our practice throughout the paper.

nuclei by α -particles of energy smaller than the height of the potential barrier cannot be interpreted satisfactorily, for the maximum range of the emitted protons may correspond not to the capture of the α -particle of maximum range, but to the capture of an α -particle of unknown (lower) range which enters the nucleus by a false level. It may be noted that this question does not affect the previous consideration of the disintegration of boron and nitrogen, for the potential barrier against the α -particle for these nuclei is probably less than the energy of the polonium α -particle. For nuclei of higher atomic number than these we must interpret the experimental results with some reserve.

Considering now the energy changes in the disintegration of aluminium we find that Pose's measurements of the resonance groups lead to a gain of energy of 2.5×10^6 e-volts in one case, of 2.4×10^6 in the other. If we attribute the maximum proton range of 65 cm. observed in our experiments to the α -particle of maximum range (3.7 cm.) incident on the aluminium, we find $Q = +2.3 \times 10^6$ e-volts, a fair agreement. This disintegration is undoubtedly a case of capture of the α -particle, in which Al_{27} is transformed into Si_{30} .

The main group of protons from aluminium, of range 32 cm. for an incident α -particle of 3.7 cm. range, corresponds to a value of Q of -0.1×10^6 e-volts (taking the average of all observations). This group has been ascribed* to a disintegration without capture of the α -particle. Such an interpretation seems difficult to sustain, not only on account of the shape of the absorption curve, but mainly because of arguments based on the mass defects of nuclei. If this group is the continuous spectrum then the disintegration $\text{Al}_{27} \rightarrow \text{Mg}_{26}$ takes place with very little change of energy and Mg_{26} has the same mass defect as Al_{27} . This seems most improbable (cf. fig. 13). Further, we should have an aluminium nucleus in which one proton was at a level of -0.1×10^6 volts, and the α -particles at (roughly) -2.5×10^6 e-volts. The total energy defect of aluminium is not known, but it cannot be very different from about 40 to 45×10^6 e-volts (fig. 13). To account for the large defect we should have to put the remaining pair of protons in an exceedingly deep level. It seems more plausible to ascribe this group of protons also to capture disintegration, in which an excited Si_{30} nucleus is formed, which will pass to the stable Si_{30} , given by the other capture process, with the emission of γ -rays of $h\nu = 2.4 \times 10^6$ e-volts.

There is then no evidence in these experiments of a continuous spectrum of protons. The range of this spectrum cannot be greater than 16 cm. in the forward direction, that is, the loss of energy in disintegration without capture

* Cf. Chadwick and Gamow, *loc. cit.*, and Pose, *loc. cit.*

must be greater than 1.3×10^6 e-volts. There is some indication in the early experiments of Rutherford and Chadwick that the continuous spectrum of aluminium disintegrated by α -particles of 7 cm. range cannot have a range in the forward direction greater than about 30 cm. Such a range would lead to a loss of energy in the disintegration of about 2.5×10^6 e-volts. We may take this as a minimum value for the depth of the first proton level of aluminium. The mass defect obtained for Mg_{26} from this will be a maximum value.

The evidence about the aluminium nucleus may be summed up as follows. Experiments on the scattering of α -particles by aluminium suggest that the height of the potential barrier (for an α -particle) is about 7.4×10^6 e-volts.* Pose's experiments quoted above give two "false" levels of 4.8×10^6 and 3.9×10^6 e-volts. The first proton level is probably at a greater depth than -2.5×10^6 e-volts, and, from a general consideration of mass defects, the α -particle level may be about -5×10^6 e-volts. More experimental evidence is clearly required.

Fluorine and Sodium.—The absorption curves of the disintegration protons from these elements are difficult to explain. They show no indication of the presence of discrete groups. We must suppose, until we have further evidence, that there may be several groups which have not been resolved under the conditions of our experiments.

Assuming that the maximum range of the protons corresponds to a disintegration effected by the α -particle of maximum range used in the experiments, and not to a resonance phenomenon, we find that in the case of fluorine there is a gain of energy in the disintegration of 1.8×10^6 e-volts, and in the case of sodium a gain of 1.0×10^6 e-volts. Both these disintegrations must take place with capture of the α -particle and correspond to changes $\text{F}_{19} \rightarrow \text{Ne}_{23}$ and $\text{Na}_{23} \rightarrow \text{Mg}_{26}$. The mass defects of Ne_{23} and Mg_{26} deduced from these results (assuming the mass defect of Na_{23}) are shown in fig. 13. It is to be noted that these will be minimum values for the mass defects.

Phosphorus.—The disintegration observed for phosphorus is clearly one of capture. The energy change Q is $+0.5 \times 10^6$ e-volts, assuming again that the effect is due to α -particles of the maximum range present. The value deduced for the mass defect of S_{34} is shown in fig. 13. If the observed disintegration of phosphorus were due to a resonance between the nucleus and a slower α -particle the true energy change will be greater than the above, and the mass defect of S_{34} will be correspondingly larger.

* Cf. Rutherford, Chadwick and Ellis, "Radiations from Radioactive Substances," p. 278, Cambridge University Press.

§ 6. *General Discussion.*

In the above examination we have found it possible to explain all our experimental results (with the exception of those for fluorine and sodium) by the assumption of definite levels for the protons and the α -particles in a nucleus. In making further deductions about the structure of nuclei we have assumed that a nucleus consists of electrons, protons, and α -particles, the number of the latter being as large as possible; that all the α -particles of a stable nucleus are in the same energy level, and that not more than two protons can be put into the same proton level. These assumptions seem to be sufficient to satisfy such facts as are at present known.

We have supposed that two types of disintegration are possible, one in which the α -particle is captured by the nucleus, and the other in which a proton is ejected without capture of the α -particle. All the groups of disintegration protons observed in our experiments have been ascribed to capture disintegration. The only experimental evidence for disintegration without capture has been derived from the experiments of Bothe and Fränzl on the disintegration of boron. It is most important to find the continuous spectrum of protons corresponding to disintegration without capture, for this gives immediately the level of the proton in the nucleus. As we have seen, the evidence to be obtained from the line spectrum is not so simple and definite, for this is concerned with the general change in the α -particle levels during the disintegration as well as with the proton level of the original nucleus.

It may be possible to find evidence of disintegration without capture in another way. If we examine the α -particles scattered through large angles by, say, a B_{10} nucleus, we should find two groups of particles; one group with an energy corresponding to the momentum and energy relations for the normal collision, and a second group, corresponding to α -particles which have disintegrated the nucleus, with a maximum energy lower than the first by the amount necessary to remove the proton, in this case about 1.4×10^6 e-volts. In other words, there will be a group of elastically scattered particles and a group of inelastically scattered particles. The phenomenon is analogous to the scattering of electrons by an atom.

In some cases, notably in the case of boron, the disintegration by capture takes place in two ways, and it is necessary to assume that two types of the new nucleus can be formed. The type which is formed with the smaller release of energy must change later into the second, more stable type, with the emission of energy in the form of γ -radiation. In the majority of disintegrations by

capture of B_{10} , an excited C_{12} nucleus is first formed, and the stable C_{12} nucleus is produced relatively seldom in a single step. The same is true in the case of aluminium. It is as if a nuclear transformation is more likely to take place in a series of steps of small energy changes than in a single step of large energy change. The emission of γ -rays from light elements bombarded by α -particles has been detected by Mr. H. C. Webster in this laboratory and more particularly by Bothe and Becker.* The latter have estimated the energy of the γ -rays, and their results agree with our deductions in the two cases, boron and aluminium, for which we have experimental data.

If the mass of a nucleus which can be artificially disintegrated is known we can deduce, from the values of the energy changes in the disintegration, the masses of the new nuclei which are formed in the process. Since a very small mass corresponds to a large amount of energy no sensible error can be introduced by the disintegration experiments. We can thus extend Aston's mass measurements, and in some cases obtain an independent check on them. Unfortunately, most of the nuclei formed in disintegration experiments have not been measured in the mass spectrograph, and many of them are indeed of rare occurrence. A notable exception is the neon isotope Ne_{22} , and for this our result is very different from Aston's. We are informed by Dr. Aston that the measurement of the mass of Ne_{22} may be inaccurate owing to technical difficulties. Fig. 13 gives the results of Aston's mass measurements of the lighter elements and our deductions from the disintegration experiments, in terms of the mass defects of the nuclei. The masses of sodium and aluminium have not been measured in the mass spectrograph. We have assumed that the mass defects of these nuclei lie on the curve drawn for the mass defects of $4n + 3$ bodies. It must be noted that the value for Mg_{26} deduced from sodium is a minimum estimate, while that deduced from aluminium is a maximum estimate for the mass defect.

A point of some interest arises from a consideration of the mass defects of the very light elements. It is well known that no certain evidence of the disintegration of lithium or beryllium has been obtained, although it is to be expected that, generally speaking, the lighter the element the easier its disintegration should be. An explanation can now be given in terms of the mass defects. Lithium consists mainly, to about 93 per cent., of the isotope Li_7 . This would give by capture disintegration (which is the easier to observe) a beryllium nucleus of mass 10. If this nucleus is to exist it must have a mass defect less than that of boron of mass 10. An inspection of fig. 13 shows that

* Bothe and Becker, *loc. cit.*

the change $\text{Li}_7 \rightarrow \text{Be}_{10}$ can take place only with a large absorption of energy, nearly 8×10^6 e-volts. Even with the fastest α -particles at our disposal, the disintegration of Li_7 would therefore be very difficult to observe. The other lithium isotope Li_6 would change with capture of an α -particle and emission of a proton to Be_9 . This transformation also requires a supply of energy, in this case about 1.1×10^6 e-volts. If the mass defects given in fig. 13 are accurate it should be possible to observe the disintegration $\text{Li}_6 \rightarrow \text{Be}_9$ under good experimental conditions. It must be remembered, however, that for deductions of this kind the masses of the nuclei must be known very accurately, for a mass of 0.001 corresponds to an energy of nearly 1×10^6 volts. In the case of beryllium, a capture disintegration leads to the formation of a nucleus of boron of mass 12. This must have a mass defect less than that of C_{12} , and hence the disintegration $\text{Be}_9 \rightarrow \text{B}_{12}$ will require a supply of energy of at least 2×10^6 e-volts.

There remain some questions of a general nature. The experimental evidence indicates that the protons resulting from a capture disintegration are emitted fairly uniformly in all directions. The only evidence on disintegration without capture suggests that in this case the protons are emitted mainly in the direction of the incident α -particles. If this is true in general the distribution with angle will provide a valuable criterion for the recognition of the types of disintegration, but it may be that the distinction only holds in the case of very light elements when the recoiling nucleus has a relatively large velocity. There is also the question mentioned in the discussion of the disintegration of aluminium—whether α -particles of smaller energy than corresponds to the height of the potential barrier have any appreciable chance of penetrating into the nucleus and causing disintegration. (We disregard here the occurrence of resonance.) Allied to this is also the question whether the protons emitted in disintegration pass to any appreciable extent through the potential barrier of the nucleus or whether they must always require sufficient energy to leap the barrier if they are to escape. Both these questions are of great importance in the general problem of artificial disintegration, but they must be left for further experiment to decide. It may be noted here that if there is a sudden change in the chance of capture when the energy of the α -particle falls below the height of the potential barrier, it should be possible to obtain, from the energy distribution of the protons emitted under suitable conditions, definite information about the height of the potential barriers of nuclei.

Summary.

The protons emitted by certain elements when bombarded by α -particles have been examined by an electrical method. Polonium was used as the source of α -particles, and the emitted protons were observed both in the direction of the incident α -particles and at right angles to it.

It was found that, except in the cases of fluorine and sodium, the disintegration protons consisted of distinct groups. The origin of these groups is explained on the assumption that the protons and α -particles contained in a nucleus are in definite energy levels. Information about the position of these levels is obtained from an examination of the experimental results. The mass defects of certain nuclei formed in the disintegration processes are deduced. Some points of general interest in the problem of artificial disintegration are discussed.

It is a pleasure to acknowledge here our indebtedness to Dr. G. Gamow for his help in the interpretation of our experiments.

We also acknowledge gratefully the grants received by two of us from the Department of Scientific and Industrial Research.

The Behaviour of Water with Change of Temperature and with Addition of Electrolytes as Studied by the Raman Effect.

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(Communicated by O. W. Richardson, F.R.S.—Received July 21, 1930.)

[PLATE 7.]

1. *Introduction.*

A detailed investigation of the Raman bands for water in the solid and liquid states was first made by the author.* Therein it was found that both ice and water give three sets of bands at $\lambda\lambda$ 4170, 4680 and 5105 A.U. respectively, corresponding to exciting mercury lines at $\lambda\lambda$ 3650, 4047 and 4358 A.U. The positions of these bands were not identical for ice and water. The former was found to give sharper bands and their shift from the original exciting

* 'Ind. J. Phys.,' vol. 3, p. 131 (1928).

line was less than for water. The mean infra-red absorptions corresponding to the bands for ice and water were $3.1\ \mu$ and $2.99\ \mu$ respectively.

The above work was done with an instrument of very small dispersion, so that the structure of the band in either case could not be studied at all.

Working with a spectrograph of larger dispersion, Kohlrausch and Dadiou* found that these bands were not single but double, and they observed the same sets of bands as the author reported in the work referred to above. To determine if these bands in the different regions of the spectrum correspond to the same infra-red frequency, the author† investigated the Raman spectrum for water in the visible as well as the ultra-violet parts of the spectrum. Eleven bands were obtained due to eleven strong exciting mercury lines. The shift of each band from the corresponding original line was found, within the limits of accuracy of determining the position of the maximum of intensity of the band, to be the same for all the bands. Thus there cannot be any doubt as to the origin of these bands. They all correspond to one and the same infra-red frequency of water.

A more thorough investigation with water, ice and solutions of electrolytes was made by Ganesan and Venkateswaran.‡ They obtained with water three bands, each of which consisted of three components gradually shading into one another, the central one being the brightest. These corresponded to infra-red wave-lengths at $2.77\ \mu$, $2.90\ \mu$ and $3.13\ \mu$ respectively. They recorded observing two more faint bands corresponding to $4.25\ \mu$ and $1.82\ \mu$. For ice they got the former three bands distinctly resolved from one another, and their shifts from the exciting lines were attributed to $2.82\ \mu$, $2.95\ \mu$ and $3.13\ \mu$. Their work with nitric acid has shown equally sharp bands.

Krishnan§ has obtained, with selenite crystal, bands which were in the same position as for ice and equally sharp.

Working with concentrated solutions of electrolytes and with water at different temperatures, the author obtained results which were briefly reported previously.|| It was found that with increasing concentration of the electrolyte (nitric acid in the case reported), the three bands which merged into one another became sharper until in very strong solutions there appeared only two sharply resolved bands. With increasing temperature of water the band which was

* 'Naturwiss.', vol. 17, p. 627 (1929).

† 'Nature,' vol. 123, p. 87 (1929).

‡ 'Ind. J. Phys.', vol. 4, p. 236 (1929).

§ 'Nature,' vol. 122, p. 477 (1928).

|| 'Nature,' vol. 125, p. 600 (1930).

unresolved became sharper and shifted more and more from the exciting line. The interesting part of the observation lay not in the sharpening of the bands, but in the change in the distribution of their intensity.

Gerlach* recorded a similar observation with solutions of strong electrolytes.

Pringsheim and Schlivitch† also observed the same phenomenon with solution of lithium chloride and with change of temperature.

Meyer‡ interpreted the bands at $\lambda\lambda$ 4167 and 4678 A.U. as belonging, not to two different exciting mercury lines, but to two different characteristic frequencies of two different modifications of water molecule. But in a later communication§ this view was contradicted by him. In this, he described his work with water at high temperatures also. He found the sharpening of the water bands with increase of temperature, and attributed this to change of water molecules from the associated to the unassociated state. He also mentioned a difference in the intensity changes with temperature of the above two water bands which could not be noticed by the author.

All the work described above was only qualitative, no attempt being made to measure the intensity distribution in the bands and to interpret the changes with temperature and addition of electrolytes. The purpose of the present communication is to describe the work of the author in this direction. In the light of the previous work done in the infra-red region of the spectrum on the structure of the water band in the different states, an explanation is given of the changes observed.

The method of obtaining Raman spectra adopted by the author was described in detail in a previous communication.||

2. Results.

Fig. 2 (Plate 7) represents the spectrum of mercury arc light scattered by water in the visible and ultra-violet parts of the spectrum. The direct mercury arc spectrum is given above it in fig. 1 for comparison. There are altogether eleven Raman bands, some of which are too faint to be seen in the plate, corresponding to eleven strong exciting mercury lines. Each of these bands appears to consist of three components which gradually diffuse into one another. The central component is of maximum intensity and is

* 'Naturwiss.,' vol. 18, p. 68 (1930).

† 'Z. Physik,' vol. 60, p. 581 (1930).

‡ 'Physik. Z.,' vol. 30, p. 170 (1929).

§ 'Physik. Z.,' vol. 31, p. 509 (1930).

|| 'Proc. Roy. Soc.,' A, vol. 127, p. 279 (1930).

unsymmetrical with respect to the other two. It is nearer the band with the greatest shift from the exciting mercury line. Since, with visual micrometer measurements, it is difficult to locate the position of the maxima of intensity, microphotometric records of the whole spectrum were taken from which the positions of the maxima were easily located and their wave-lengths determined. Though visually the band appears to consist of three components, even the microphotometer could not distinctly resolve them. The results of the wave-length measurements of the intense bands are given in the following table. For each band, the wave-lengths of the two ends and the central maxima are indicated in the table.

The first and second columns in the table contain the wave-lengths of the exciting mercury lines and their wave numbers respectively. In the third and fourth columns are given the same values for the Raman bands accompanying them. The fifth column contains the wave number differences of the numbers in the second and fourth columns. The infra-red wave-lengths corresponding to these differences are represented in column 6.

λ_{Hg} in A.U.	ν_{Hg} in cm.^{-1}	λ_{R} in A.U.	ν_{R} in cm.^{-1}	$\delta \nu$ in cm.^{-1}	λ infra-red in μ .
2535-37	39436.05	2750	36353	3083	3.24
		2780	35961	3459	2.89
		2795	35768	3637	2.75
2894	34544	3176	31477	3067	3.26
		3214	31105	3439	2.91
		3236	30893	3651	2.74
2967	33694	3268	30591	3103	3.22
		3301	30285	3409	2.93
		3325	30139	3555	2.76
3022	33081	3368	29083	3398	2.94
3126-32	31981-19	3452	28960	3021	3.31
		3507	28506	3444	2.90
		3532	28305	3614	2.77
3663-50	27389-292	4124	24241	3148	3.18
		4172	23963	3389	2.95
		4232	23623	3669	2.73
4047	24705	4623	21622	3083	3.24
		4697	21282	3423	2.92
		4746	21065	3640	2.75

It is evident from the table that the maximum is not symmetrically situated with respect to the whole band. The mean values of the three positions of the band are 3.24 μ , 2.92 μ and 2.75 μ .

Figs. 3 and 8 (Plate 7) represent Raman spectra for pure water. The two bands at $\lambda\lambda$ 4172 and 4697 A.U. respectively corresponding to exciting mercury lines $\lambda\lambda$ 3663-50 and 4047 A.U. are indicated. Figs. 6 and 7 are with sodium chlorate solutions of concentrations 50 and 21 per cent. Fig. 5 is with concentrated nitric acid of 108 per cent. and fig. 4 is for sodium nitrate solution of 50 per cent. concentration. All the above concentrations are in grams per 100 c.c. of solution.

The sharpening of the water bands with increasing concentration of the electrolyte is quite clear from the plate. In nitric acid there are two distinctly resolved bands at $\lambda\lambda$ 4698 and 4732 A.U., corresponding to infra-red wavelengths of water at $2.92\ \mu$ and $2.79\ \mu$ respectively.

The variation of the intensity distribution of the band at λ 4172 was studied with increasing concentration of sodium nitrate and nitric acid. Because of the saturation of the former at about 50 per cent. concentration the study

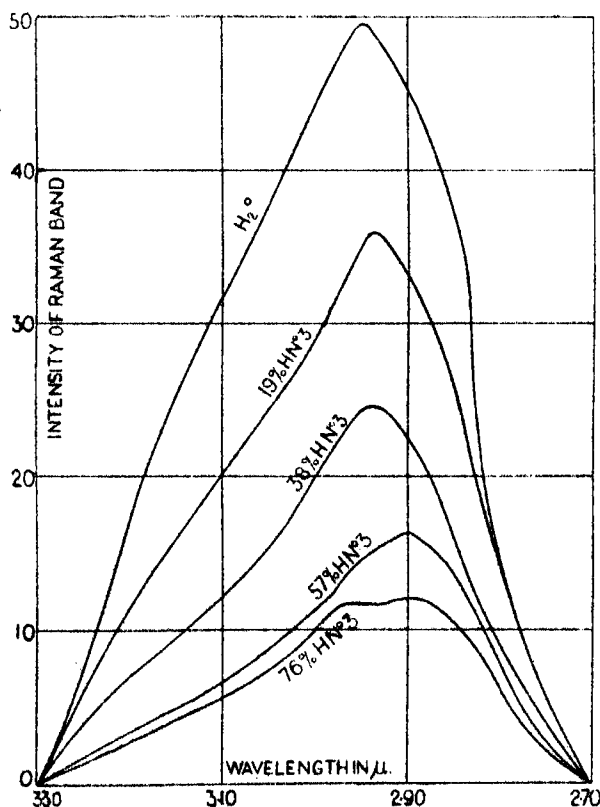


FIG. 1.—Change of the Intensity Distribution of the Raman Band for Water with addition of Nitric Acid.

could not be extended further; but with nitric acid the changes in the structure of the water bands could be made up to 76 per cent. concentration, after which absorption set in due to formation of nitrogen peroxide. The curves with the intensity distribution in the water band against the infra-red wave-length, calculated from the shift of the point in the band from the exciting mercury line, are given in fig. 1 for different concentrations of nitric acid. Because of the diminution of the percentage of water with increasing amount of nitric acid the maximum of intensity gradually diminishes.

To compare the exact form of the bands at the different concentrations, the curves at the higher concentrations are magnified to the same scale as that for water. Only three curves are given in fig. 2, representing the intensity distribution of the band for pure water and 38 per cent. and 76 per cent. concentrations of nitric acid. It is evident that in 38 per cent. nitric acid the water band is much sharper. At 76 per cent. the resolution of the two bands

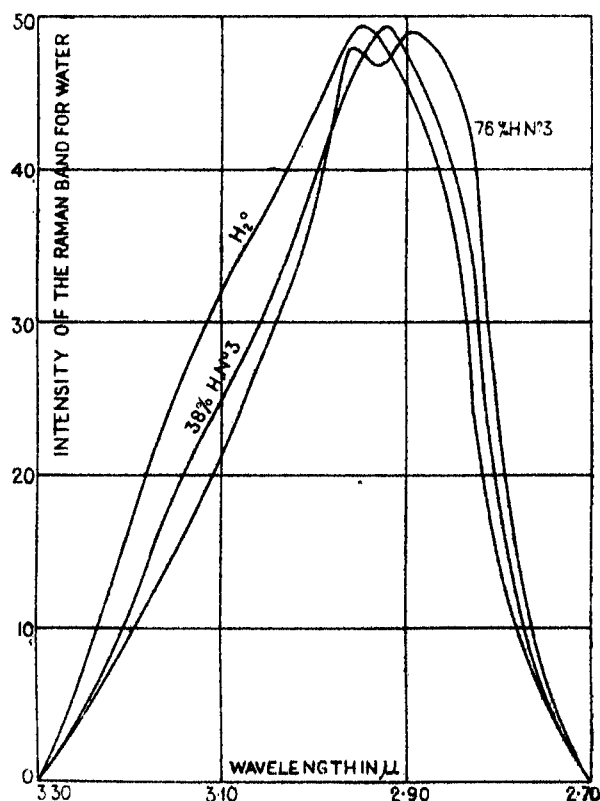
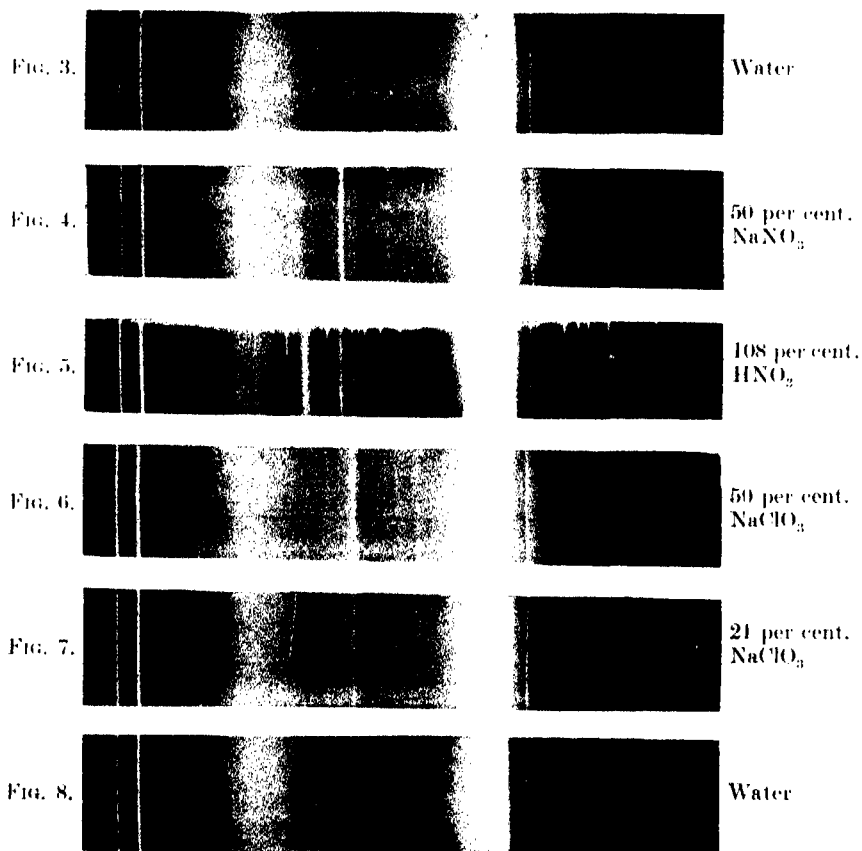


FIG. 2.—Change of the Intensity Distribution of the Raman Band for Water with addition for Nitric Acid. Bands with Nitric Acid enlarged to the same size as that with water.



λ 4697

λ 4172

corresponding to 2.97μ and 2.89μ already commences. Another notable feature of the changes is the shift of the band as a whole towards the short wave-length side with increasing concentration. Hence the position of the latter in 108 per cent. HNO_3 is 2.79μ , whereas that at 76 per cent. is at 2.89μ .

Fig. 3 represents the curves showing the distribution of intensity in the water band at 14°C. and 75°C. The spectra are exposed for the same time under identical conditions. Thus any changes in the Raman band must be

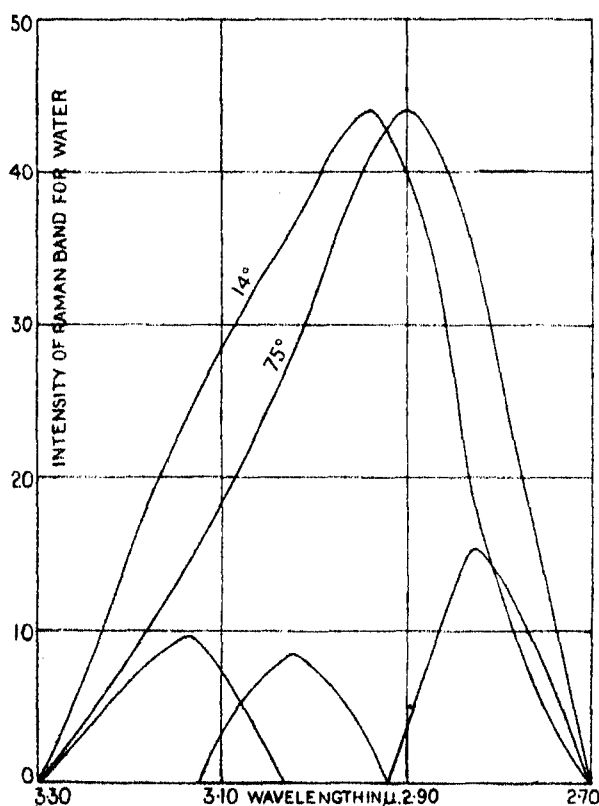


FIG. 3.—Change in Intensity Distribution of the Raman Band for Water with Temperature.

due to change in the constitution of water on account of change of temperature. There are two important features of these changes. The first is the diminution in its intensity on the longer wave-length side and the second the increase on the shorter wave-length side with increasing temperature.

3. Discussion.

Collins* found similar changes with temperature in the infra-red absorption bands of water. The shift in the position of the maximum of the band towards the shorter wave-length side was clearly noted by him. He did not work with the one corresponding to $2.94\ \mu$, but with bands lying between 0.7 and $2.1\ \mu$. Hettner† investigated the infra-red absorption bands of water-vapour. He found strong diffuse bands, the wave-lengths of whose maxima were approximately $1.36\ \mu$, $1.84\ \mu$, $2.70\ \mu$ and $6.30\ \mu$. Of these, that corresponding to $2.70\ \mu$ only is obtained by the author in the Raman spectrum. Ganesan and Venkateswaran reported having observed the bands corresponding to $1.82\ \mu$ and $4.25\ \mu$, but the author could not detect them. No other worker on the Raman spectrum for water has mentioned having found these bands.

On comparing the bands for water and ice, the author found that in ice they correspond to a longer infra-red wave-length than in water. In water-vapour Hettner found the maximum of the band at $2.70\ \mu$. The band for ice corresponds to $3.10\ \mu$, but in water the maximum is at $2.94\ \mu$.

The difference in the positions of the bands for the three different states can be explained if water is supposed to consist of three kinds of molecules, single H_2O , double $(\text{H}_2\text{O})_2$ and triple $(\text{H}_2\text{O})_3$. The relative proportions of these depend on the physical condition of water. It may be reasonable to suppose that, in ice, the double and triple molecules are more in proportion than in the liquid and vapour states. In the latter it may consist entirely of single molecules, which give rise to the band at $2.70\ \mu$ observed by Hettner in the infra-red absorption. Thus the remaining two maxima at $2.95\ \mu$ and $3.13\ \mu$ obtained by Ganesan and Venkateswaran in ice may be attributed to the double and triple molecules respectively. The feeble intensity of the band at $2.82\ \mu$ in ice observed by the above authors indicates the small proportion of single molecules in ice. While in water the maximum of intensity is at $2.94\ \mu$, in ice the two resolved bands $2.95\ \mu$ and $3.13\ \mu$ are equally bright. This is an indication of the larger proportion of triple molecules in ice than in water.

From the above it is now easy to explain the changes in the intensity distribution of the water band with temperature. With increasing temperature, the intensity on the shorter wave-length side increases and that on the longer side diminishes. The part of the band on the former side is due to single

* 'Phys. Rev.', vol. 26, p. 771 (1925).

† 'Ann. Physik', vol. 55, p. 476, (1918).

molecules and that on the latter due to triple molecules, as has been assumed in the previous paragraph. The above changes in the intensity distribution show that, with increasing temperature, the number of single molecules in water increases and that of triple molecules diminishes. With the above data it is difficult to determine the nature of the change in the proportion of double molecules; but from the gradual shift of the maximum of the band from 2.94μ towards 2.70μ it appears that the double molecules also diminish.

It would have been interesting to determine quantitatively the relative proportions of the different types of molecules in the various stages, but the bands due to them overlap so much that their analysis is difficult. A study of the differences in the intensity of the bands at 14°C. and 75°C. , however, has confirmed the above views regarding the changes with temperature in the intensity distribution. The differences are plotted at the bottom of fig. 3. The curve giving the intensity differences on the short wave-length side has a single maximum and is approximately symmetrical, but that on the longer side has two maxima. A rough analysis of the latter has resulted in the two simple curves given on the longer wave-length side in fig. 3. The three curves correspond to the changes in the amounts of the three different types of molecules in water. The fact that the difference at about 3.13μ is more than that at 3.02μ shows that the triple molecules which have their band at the longer wave-length diminish with temperature more than the double molecules. The curve with maximum at 2.83μ is higher than either of the other two. This shows that the increase in the proportion of single molecules with rise of temperature is much more than the diminution of either the double or triple molecules. This is obvious because the double and triple molecules both change into single with rise of temperature. Thus the study of the curves confirms the general explanation given above of the behaviour of the water bands.

There is an error of about 10 per cent. in the estimation of the intensities of the bands. Thus the curves giving the differences of the two bands at the two different temperatures are much more in error. Hence a comparison of the intensities of the three lower curves may not give exactly the changes in the proportions of single, double and triple molecules. Also it is not known how far the ratios of the intensities are the same as the ratio of the numbers of the different types of molecules. Hence no attempt is made to arrive at quantitative values of the above changes.

From these observations of the temperature effect it is easy to explain the

changes, indicated in fig. 1, of the intensity distribution of the water band with addition of electrolyte. In the initial stages the band shifts to the short wave-length side as with increasing temperature. This may be due to the diminution of the proportion of the triple and increase of the single water molecules. In the later stages, however, a second maximum begins to develop, as will be seen from the band for 76 per cent. nitric acid, which does not appear at all in the temperature phenomenon. The reason for this may be the formation of hydrates. The water molecules, instead of combining among themselves, begin to associate with the molecules of the electrolyte. The position of the hydrate band cannot be the same as for water; but the heaviness of the ions or molecules with which the water molecule combines, results only in a small shift of the water band. Hence we get the second maximum in nitric acid at about 2.94μ . On account of the superposition of the band due to the hydrate on that due to water alone it is difficult to say how far the water uncombined with the electrolyte is associated into double molecules; but it can be mentioned with certainty that the triple molecules diminish with increasing amount of the electrolyte.

To attempt at an exact analysis of the bands it is necessary to work with water at temperatures much higher than 100°C ., where the number of double and triple molecules may be negligible in comparison with the single. Also exact intensity work with Raman bands in ice and in water-vapour is also required.

4. *Summary.*

1. A brief account of the previous work on the Raman bands for water is given.

2. Exact wave-length measurements of the bands in the visible and ultra-violet regions of the spectrum are made. The maximum of the water band lies at mean wave-length 2.92μ and the two extremes lie at about 2.75μ and 3.24μ .

3. Study of the band with addition of electrolyte has shown that it gets sharper and the maximum shifts towards 2.70μ . With high concentrations, a second maximum appears at about 2.79μ .

4. Change of temperature of the water has shown that the intensity on the long wave-length side diminishes and on the short wave-length side increases as with addition of electrolyte.

5. This is explained as being due to changes in the proportions of the single, double and triple molecules, which water is supposed to consist of. The diminution in the intensity on the long wave-length side is attributed to

diminution of the amount of triple molecules which give rise to the band here. The increase on the short wave-length side is explained as due to increase in single water molecules. Comparison of the work in the infra-red by others has confirmed these observations.

6. The changes in the intensity distribution of the band with addition of electrolytes is also explained by changes in the proportions of triple and single molecules. The development of the second maximum with concentrations higher than 76 per cent. of nitric acid is attributed to formation of hydrates.

The work was partly done in King's College, London, and partly at Physisch Laboratorium, Utrecht. The author is extremely grateful to Prof. O. W. Richardson and to Prof. L. S. Ornstein for the help and encouragement they gave during the course of this work.

Quantum Mechanics of Electrons in Crystal Lattices.

By R. de L. KRONIG and W. G. PENNEY, University of Groningen.

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Introduction.—Through the work of Bloch our understanding of the behaviour of electrons in crystal lattices has been much advanced. The principal idea of Bloch's theory is the assumption that the interaction of a given electron with the other particles of the lattice may be replaced in first approximation by a periodic field of potential. With this model an interpretation of the specific heat,* the electrical and thermal conductivity,† the magnetic susceptibility,‡ the Hall effect,§ and the optical properties|| of metals could be obtained. The advantages and limitations inherent in the assumption of Bloch will be much the same as those encountered when replacing the interaction of the electrons in an atom by a suitable central shielding of the nuclear field, as in the work of Thomas and Hartree.

* Bloch, 'Z. Physik,' vol. 52, p. 555 (1928).

† Bloch, 'Z. Physik,' vol. 52, p. 555 (1928), vol. 53, p. 216 (1929), and vol. 59, p. 208 (1930); Peierls, 'Ann. Physik,' vol. 4, p. 121 (1930), and vol. 5, p. 244 (1930).

‡ Bloch, 'Z. Physik,' vol. 53, p. 216 (1929).

§ Peierls, 'Z. Physik,' vol. 53, p. 255 (1929).

|| Kronig, 'Proc. Roy. Soc.,' A, vol. 124, p. 409 (1929).

In the papers quoted a number of general results were given regarding the behaviour of electrons in any periodic field of potential. To obtain a clearer idea of the details of this behaviour with a view to the application in special problems, however, it appeared worth while to investigate the mechanics of electrons in periodic fields of potential somewhat similar to those met with in practice and of such nature that the energy values W and eigenfunctions ψ of the wave-equation can actually be computed. It is the purpose of this article to discuss a case where the integration is possible. In Section 1 the energy values and in Section 2 the wave-functions in their dependence on the binding introduced by the potential field are discussed for the one dimensional problem. In Section 3 the matrix elements of the linear momentum, which furnish the electric current associated with the various stationary states as well as the probability of radiative transitions between these states, are evaluated. In Section 4 the results are extended to the three dimensional case and those features considered which one may expect to find in the case of more general periodic fields of potential. Section 5 deals with some applications to physical problems.

1. *The Energy Values.*—The potential field which we shall consider is essentially that shown in fig. 1. Later on we shall pass to the limit $b = 0$

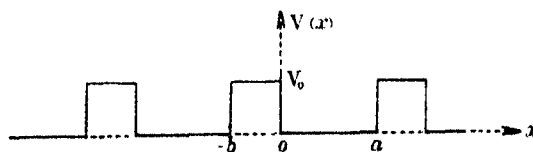


FIG. 1.

and $V_0 = \infty$ as this makes the results mathematically simpler without essentially altering their character, but to begin with we leave both b and V_0 finite. The wave-equation of the problem is given by

$$\frac{d^2\psi}{dx^2} + \kappa^2 [W - V(x)] \psi = 0, \quad \kappa^2 = \frac{8\pi^2m}{h^2}, \quad (1)$$

and following Bloch* we enquire after the solutions ψ which are periodic over a distance $L = G(a + b)$, where G is a large integer. As he has shown, these solutions must be of the form

$$\psi(x) = u(x) e^{i\alpha x}, \quad \alpha = 2\pi k/L, \quad (2)$$

where k is any integer and $u(x)$ a function periodic in x with the period $(a + b)$. To find $u(x)$ we can hence confine ourselves to one period of the lattice, say

* Bloch, 'Z. Physik,' vol. 52, p. 555 (1928).

from $x = -b$ to $x = a$, and moreover, since we later shall make $V_0 = \infty$, we may assume $0 < W < V_0$. Substituting the expression (2) in equation (1) imposes on u in the range $-b \leq x \leq 0$ the condition

$$\frac{d^2u}{dx^2} + 2i\alpha \frac{du}{dx} - (\alpha^2 + \gamma^2)u = 0$$

with the solution

$$u = Ae^{(-i\alpha+\gamma)x} + Be^{(-i\alpha-\gamma)x}, \quad (3)$$

while in the region $0 \leq x \leq a$ we have

$$\frac{d^2u}{dx^2} + 2i\alpha \frac{du}{dx} - (\alpha^2 - \beta^2)u = 0$$

with the solution

$$u = Ce^{i(-\alpha+\beta)x} + De^{i(-\alpha-\beta)x}. \quad (4)$$

Here β and γ are given by

$$\beta = \kappa \sqrt{W}, \quad \gamma = \kappa \sqrt{V_0 - W}. \quad (5)$$

In particular β and γ are real quantities and may be assumed positive without loss of generality.

The constants A, B, C, D are to be so chosen that the solutions in the two regions have the same value and the same first derivative for $x = 0$, while from the periodic nature of u it follows that the solution (3) and its first derivative for $x = -b$ shall be equal respectively to the solution (4) and its first derivative for $x = a$. The four linear homogeneous equations resulting for the constants from these requirements are

$$\begin{aligned} A+B &= C+D, \\ (-i\alpha+\gamma)A + (-i\alpha-\gamma)B &= i(-\alpha+\beta)C + i(-\alpha-\beta)D, \\ Ae^{(i\alpha-\gamma)b} + Be^{(i\alpha+\gamma)b} &= Ce^{i(-\alpha+\beta)a} + De^{i(-\alpha-\beta)a} \\ (-i\alpha+\gamma)Ae^{(i\alpha-\gamma)b} + (-i\alpha-\gamma)Be^{(i\alpha+\gamma)b} &= i(-\alpha+\beta)Ce^{i(-\alpha+\beta)a} \\ &\quad + i(-\alpha-\beta)De^{i(-\alpha-\beta)a}, \end{aligned}$$

and can be satisfied only if the quantities β and γ , which according to equation (5) are directly related to the energy value W , satisfy the relation

$$\frac{\gamma^2 - \beta^2}{2\beta\gamma} \sinh \gamma b \sin \beta a + \cosh \gamma b \cos \beta a = \cos \alpha (a+b).$$

Passing now to the limit where $b = 0$ and $V_0 = \infty$ in such a way that $\gamma^2 b$ stays finite and calling

$$\lim_{\substack{b \rightarrow 0 \\ \gamma \rightarrow \infty}} \frac{\gamma^2 ab}{2} = P,$$

this relation becomes

$$P \sin \beta a / \beta a + \cos \beta a = \cos \alpha a, \quad (6)$$

a transcendental equation for βa .

To discuss the roots of this equation we have plotted its left-hand side as a function of βa in fig. 2, assuming for P the value $3\pi/2$. The values of βa

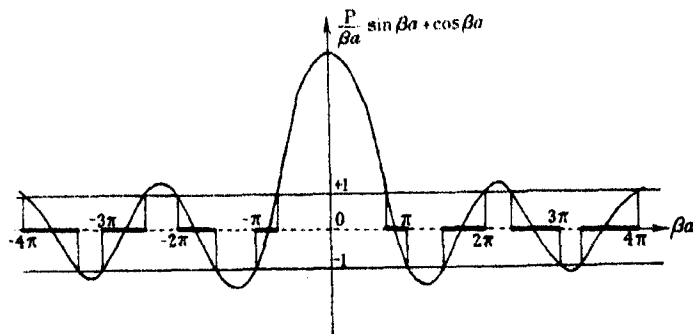


FIG. 2.

satisfying equation (6) are obtained as the projections on the βa -axis of the intersections of the curve with a straight line drawn at the distance $\cos \alpha a$ parallel to this axis. Since $\cos \alpha a$ lies between -1 and $+1$, and since the ordinates of the maxima of the curve have an absolute magnitude greater than 1 , then, upon varying α by giving k different values, the curve is found to consist of the portions between the parallels ± 1 on which there lie intersections and the remaining portions outside these parallels on which there lie no intersections. By projection the βa -axis too is divided into portions containing permissible values of βa (drawn heavily in fig. 2) and portions not containing such values. Letting L approach infinity allows us according to equation (2) to vary α continuously, and the permissible values of βa will then fill the heavily drawn portions of the βa -axis continuously. *The energy values which an electron moving through the lattice may have, hence form a spectrum consisting of continuous pieces separated by finite intervals.*

It is of interest to study the influence of P upon this spectrum. If P vanishes, the curve of fig. 2 goes over into $\cos \beta a$, the forbidden intervals of the βa -axis disappear, and we have one continuous spectrum of all energy values from 0 to ∞ . This is the limiting case of *free electrons*. Increasing P we obtain the forbidden intervals, the ratio of the length of these intervals to that of the adjoining allowed portions decreasing as we pass to large values of βa . We may say that fast electrons have less trouble to pass the potential

barriers than slow electrons and can be considered more nearly as free. Letting P approach infinity reduces the allowed portions of the βa -axis to the points $n\pi$ ($n = \pm 1, \pm 2, \dots$). The energy spectrum now becomes discrete, the energy values

$$W = n^2 \hbar^2 / 8ma^2, \quad (n = 1, 2, \dots)$$

being those of an electron confined to move between two impenetrable potential barriers at a distance a apart. The electrons are caught between the potential walls, they have become bound.

Fig. 3 shows the change in the energy spectrum during the transition from the case of free to that of bound electrons. In the region $0 \leq P \leq 4\pi$, $P/4\pi$ has been chosen as abscissa, while for $4\pi \leq P \leq \infty$ $4\pi/P$ is used. The shaded area represents the allowed values of $(\beta a/\pi)^2$.

2. *The Wave-functions.*—We come now to consider the wave-functions of our problem. Since b in the limit is reduced to zero, we are only concerned with the solution (4). Solving the linear equations for the constants A, B, C, D in this limiting case gives us

$$D = -C \frac{1 - e^{-i(a-\beta)a}}{1 - e^{-i(a+\beta)a}}. \quad (7)$$

u is given by equation (4) in the cell extending from 0 to a , while in the cell extending from ra to $(r+1)a$ it will be given by

$$u = Ce^{i(-a+\beta)(x-ra)} + De^{i(-a-\beta)(x-ra)},$$

being periodic with the period a . According to equation (2) ψ in this cell will then be given by

$$\psi = Ce^{i\beta x + ir(a-\beta)a} + De^{-i\beta x + ir(a+\beta)a}, \quad (8)$$

with C and D related by equation (7). If we require that ψ be normalised over a distance equal to its period L , we must have

$$CC^* = \frac{1}{2L} \frac{1 - \cos(\alpha + \beta)a}{1 - \cos \alpha a \cos \beta a + \frac{1}{P}(\cos \alpha a - \cos \beta a)^2}, \quad (9)$$

the asterisk denoting the conjugate.

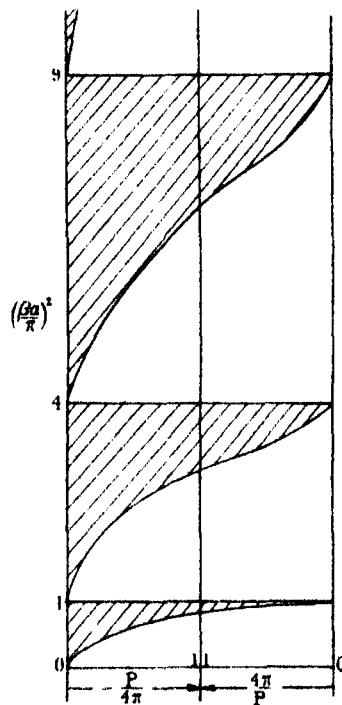


FIG. 3.

From equation (6) it appears that if with a given permissible value of βa a certain value of αa satisfies this equation, then also $\alpha a + 2n\pi$ and $-\alpha a + 2n\pi$ (n an integer) will satisfy it. We see, however, from equations (7) and (8) that by substituting $\alpha a + 2n\pi$ for αa we do not obtain any new wave-functions, while substituting $-\alpha a + 2n\pi$ for αa we get the same wave-function as that belonging to $-\beta a$, $-\alpha a$. We may hence, without loss of generality, accept the convention that if $n\pi \leq \beta a \leq (n+1)\pi$, we shall associate with it that value of αa for which $n\pi \leq \alpha a \leq (n+1)\pi$. In this way there is associated with every permissible value of βa one and only one value of αa , and we may use α to distinguish the stationary states.

We shall next investigate the influence of the value of P on the wave-functions. If we make P vanishingly small, then according to the convention just introduced βa will equal αa , and according to equation (7) D will vanish excepting for $\alpha a = n\pi$, in which case $D = \pm C$. The wave-functions according to equation (8) will go over into $e^{\pm i\alpha x}$ excepting for the special case just mentioned, in which they become equal to $\sin \alpha x$ and $\cos \alpha x$ so that we obtain the *wave-functions of free electrons*. At the same time the significance of α becomes apparent. For P approaching infinity, β takes the values $n\pi$, $D = -C$ according to equation (7), and we get from equation (8) the *wave-functions of electrons confined in their motion between impenetrable potential walls* at a distance a apart.

If we let L increase, the energy values, as mentioned before, come closer together, and for very large values of L we may enquire after the *density distribution of the energy values* in the allowed regions of βa . According to equation (2) this is evidently given by

$$\rho(\beta a) = \frac{L}{2\pi} \frac{d\alpha}{d\beta} = \frac{L}{2\pi \sin \alpha a} \left(\frac{P}{(\beta a)^2} \sin \beta a - \frac{P}{\beta a} \cos \beta a + \sin \beta a \right)$$

with $\rho(\beta a)$ so normalised that

$$\int_{(\alpha\beta) \text{ min.}}^{(\beta a) \text{ max.}} \rho(\beta a) d\beta a = \frac{L}{2},$$

the integration extending over any one of the allowed regions of βa . Fig. 4 shows $\rho(\beta a)/L$ in the first of these for a value $P = 3\pi/2$, while for free electrons ($P = 0$) one obtains instead a horizontal line with an ordinate $1/2\pi$ for all values of βa . The binding has thus the effect of concentrating the stationary states at the limits of an allowed region.

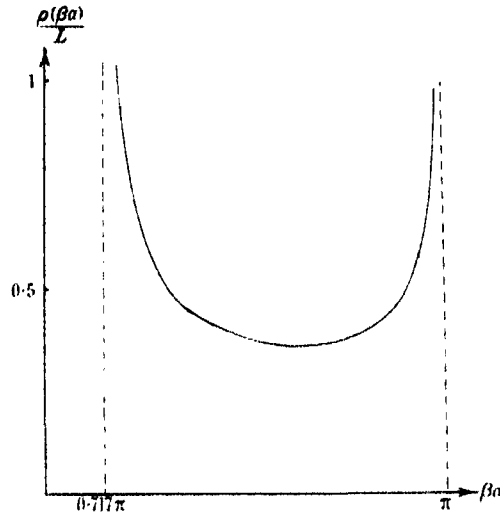


FIG. 4.

3. *The Linear Momentum.*—According to quantum mechanics the matrix elements of the linear momentum of an electron belonging to two stationary states α and α' are given by

$$p(\alpha, \alpha') = \frac{h}{2\pi i} \int \psi_{\alpha}^* \frac{\partial \psi_{\alpha'}}{\partial x} dx,$$

the integration extending over one period L of the functions ψ_{α} and $\psi_{\alpha'}$. Introducing for ψ_{α} and $\psi_{\alpha'}$ their expressions given by equations (7), (8), (9) and performing the integration it is found that $p(\alpha, \alpha')$ vanishes unless αa and $\alpha' a$ differ by an integral multiple of 2π . Thus if the state α lies in the first allowed region of the positive βa -axis, then $p(\alpha, \alpha')$ is different from zero for only one state α' in the first, one in the third, one in the fifth positive allowed region, etc., and one in the second, one in the fourth, one in the sixth negative allowed region, etc., viz., those states for which $\alpha' a = \alpha a + 2n\pi$. A simple calculation gives us for the square of the absolute value of these non-vanishing matrix elements:

$$p(\alpha, \alpha') p(\alpha', \alpha) = \left(\frac{h}{\pi a} \frac{\beta \beta'}{\beta'^2 - \beta^2} \right)^2 \times \frac{\sin^2 \alpha a (\cos \beta a - \cos \beta' a)^2}{\left[1 - \cos \alpha a \cos \beta a + \frac{1}{\beta^2} (\cos \alpha a - \cos \beta a)^2 \right] \left[1 - \cos \alpha a \cos \beta' a + \frac{1}{\beta'^2} (\cos \alpha a - \cos \beta' a)^2 \right]}. \quad (10)$$

To make the significance of equation (10) clearer we have computed from it in the first place $\pi a p(\alpha, \alpha)/h$ and plotted it in fig. 5 as a function of βa for the

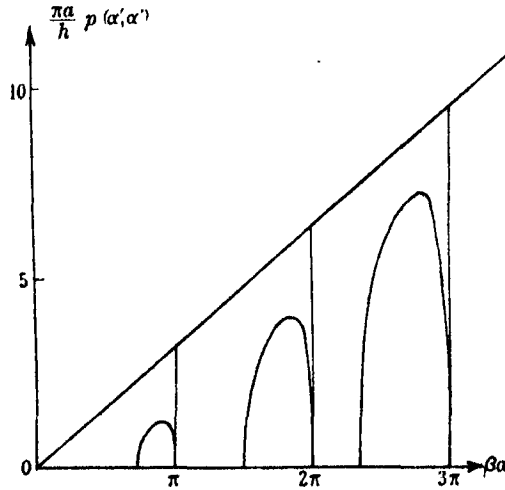


FIG. 5.

values of βa lying in the first, second and third allowed regions of the positive βa -axis, taking again P equal to $3\pi/2$. $p(\alpha, \alpha)$ represents the *time average of the linear momentum* of an electron in the stationary state α . As one easily sees

$$p(-\alpha, -\alpha) = -p(\alpha, \alpha).$$

Since the energy of the stationary states α and $-\alpha$ is the same, one may enquire if to a linear combination of the wave-functions ψ_α and $\psi_{-\alpha}$ there might correspond a linear momentum of greater absolute value, but from a simple calculation one finds that p lies then between $p(-\alpha, -\alpha)$ and $p(\alpha, \alpha)$. The straight line going through the origin in fig. 5 gives us $\pi a p(\alpha, \alpha)/h$ for the case of free electrons, showing that the potential barriers have the effect of reducing the linear momentum for a given value of the energy. Indeed they make it vanish when P approaches infinity. $p(\alpha, \alpha)$ also furnishes us the *electric current* associated with the stationary state α , whose time average is obtained by multiplying $p(\alpha, \alpha)$ by e/m , the ratio of the charge of the electron to its mass.

Furthermore we have plotted in fig. 6 the values of $\pi^2 a^2 p(\alpha, \alpha') p(\alpha', \alpha)/h^2$ as a function of βa when α is a state in the first allowed region while α' is that state

in the second negative, third positive and fourth negative allowed region (curves 1, 2 and 3 respectively) for which the above quantity is different from zero. Again P has been taken equal to $3\pi/2$. For vanishing P all the curves are reduced to zero. For infinite P the results agree with those for an electron confined to move between impenetrable walls a distance a apart. The quantities

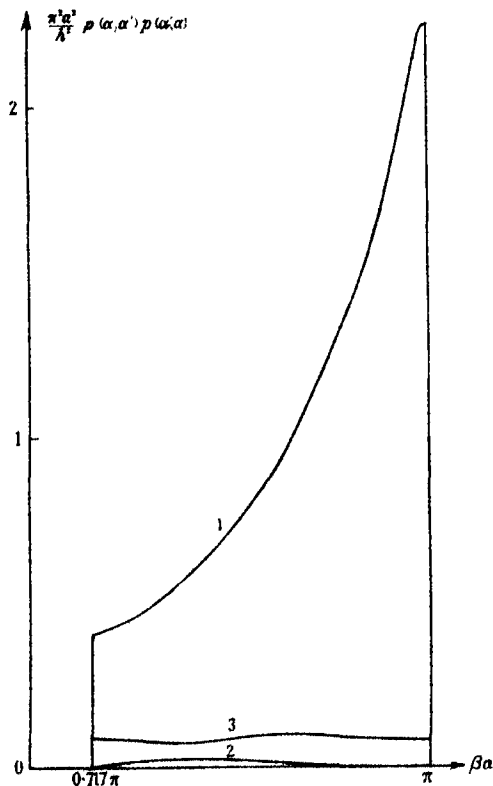


FIG. 6.

$p(\alpha, \alpha')$ determine the probability of radiative transitions between the stationary states, and one sees from fig. 6 that the transitions to the second negative region far outweigh all others.

4. *Extension of the Theory.*—The results just given can be generalised directly so as to apply to the case of a three-dimensional lattice in which the potential is the sum of three terms $V(x)$, $V(y)$, $V(z)$, each of which depends upon its co-ordinate in the same way as $V(x)$ on x in the one dimensional case. This means that the space is divided by infinitely thin potential barriers into cubical cells with an edge a . The wave-equation can then be separated

into three equations of the form (1), each involving only a single co-ordinate, viz.,

$$\left. \begin{aligned} \frac{d^2\psi_1}{dx^2} + \kappa^2[W_1 - V(x)]\psi_1 &= 0 \\ \frac{d^2\psi_2}{dy^2} + \kappa^2[W_2 - V(y)]\psi_2 &= 0 \\ \frac{d^2\psi_3}{dz^2} + \kappa^2[W_3 - V(z)]\psi_3 &= 0 \end{aligned} \right\}. \quad (11)$$

the total energy of the system and its wave-function being given by

$$W = W_1 + W_2 + W_3, \quad (12)$$

$$\psi = \psi_1 \psi_2 \psi_3 \quad (13)$$

respectively. Each of these equations can be treated in exactly the same way as equation (1). The stationary states will now be characterised by three quantities $\beta_1, \beta_2, \beta_3$, related to W_1, W_2, W_3 through equations analogous to equation (5), or by the corresponding quantities $\alpha_1, \alpha_2, \alpha_3$.

In the one-dimensional case we have seen that for $P = 0$ the energy W is a continuous function of αa , while for $P \neq 0$ W has discontinuities for $\alpha a = n\pi$ ($n = \pm 1, \pm 2, \dots$). Similarly we shall have here that for $P = 0$, W is a continuous function of $\alpha_1 a, \alpha_2 a, \alpha_3 a$, while for $P \neq 0$ the function becomes discontinuous on the surfaces $\alpha_1 a = n_1 \pi, \alpha_2 a = n_2 \pi, \alpha_3 a = n_3 \pi$ ($n_1, n_2, n_3 = \pm 1, \pm 2, \dots$). The detailed behaviour of the energy values as well as of the wave-functions when P is varied follows directly from equations (12) and (13) and the results of the previous sections. The same remark applies to the matrix elements of the linear momentum. It is interesting to note in this connection that $p_x(\alpha_1, \alpha_2, \alpha_3; \alpha_1', \alpha_2', \alpha_3')$ is different from zero only provided $\alpha_1' a = \alpha_1 a + 2n\pi, \alpha_2' a = \alpha_2 a, \alpha_3' a = \alpha_3 a$ (n integer) with similar results holding for p_y and p_z .

A number of general qualitative features encountered in the special problem discussed may be expected to occur also for other periodic fields of potential. The falling apart of the energy spectrum into continuous regions separated by finite intervals has been met with previously in the case of a potential given by $V(x) = A \cos 2ax$, discussed by Strutt,* who also mentions that a similar

* M. J. O. Strutt, 'Ann. Physik,' vol. 86, p. 319 (1928). Attention may be called here to the fact that the energy regions considered by him as allowed are just the ones excluded for translatory motion through the lattice, and *vice versa*. The energy spectra of the equations corresponding to the potential $A \cos 2ax$ and to a potential as shown in fig. 1 for the particular case $a = b$ have also been discussed in connection with problems

effect arises for any one dimensional periodic field of potential according to theorems proved by Haupt.[†] The stationary states, just as in our problem, can be characterised by a value α , the coefficient of the exponent in the function $e^{i\alpha x}$ which results from the wave-function when the potential field is reduced to zero. The energy W of the stationary states again has discontinuities at the points $\alpha a = n\pi$ ($n = \pm 1, \pm 2, \dots$). In an analogous manner the surfaces $\alpha_1 a = n_1\pi$, $\alpha_2 a = n_2\pi$, $\alpha_3 a = n_3\pi$ ($n_1, n_2, n_3 = \pm 1, \pm 2, \dots$) will be surfaces of discontinuity for the function $W(\alpha_1 a, \alpha_2 a, \alpha_3 a)$ in the general three-dimensional case.

Another result, valid for any periodic field of potential, is concerned with the matrix elements of the linear momentum $p(\alpha_1, \alpha_2, \alpha_3; \alpha'_1, \alpha'_2, \alpha'_3)$.[‡] It may be shown that these can be different from zero only if $\alpha'_1 a = \alpha_1 a + 2n_1\pi$, $\alpha'_2 a = \alpha_2 a + 2n_2\pi$, $\alpha'_3 a = \alpha_3 a + 2n_3\pi$ (n_1, n_2, n_3 integers). For the wave-functions in the two states $\alpha_1, \alpha_2, \alpha_3$ and $\alpha'_1, \alpha'_2, \alpha'_3$ according to Bloch (*loc. cit.*) are given by

$$\begin{aligned}\psi_{\alpha_1 \alpha_2 \alpha_3} &= u_{\alpha_1 \alpha_2 \alpha_3} e^{i(\alpha_1 x + \alpha_2 y + \alpha_3 z)}, \\ \psi_{\alpha'_1 \alpha'_2 \alpha'_3} &= u_{\alpha'_1 \alpha'_2 \alpha'_3} e^{i(\alpha'_1 x + \alpha'_2 y + \alpha'_3 z)},\end{aligned}$$

where the u 's are periodic in x, y, z with the period a . Introducing these functions in the expression for the matrix element of p_x , say, gives us

$$\begin{aligned}p_x(\alpha_1, \alpha_2, \alpha_3; \alpha'_1, \alpha'_2, \alpha'_3) &= \frac{h}{2\pi i} \int \psi_{\alpha_1 \alpha_2 \alpha_3}^* \frac{\partial \psi_{\alpha'_1 \alpha'_2 \alpha'_3}}{\partial x} dx dy dz \\ &= \frac{h}{2\pi i} \int u_{\alpha_1 \alpha_2 \alpha_3}^* \left[\frac{\partial u_{\alpha'_1 \alpha'_2 \alpha'_3}}{\partial x} + i u_{\alpha'_1 \alpha'_2 \alpha'_3} \right] e^{i[(\alpha'_1 - \alpha_1)x + (\alpha'_2 - \alpha_2)y + (\alpha'_3 - \alpha_3)z]} dx dy dz \\ &= \frac{h}{2\pi i} \int u_{\alpha_1 \alpha_2 \alpha_3}^* \frac{\partial u_{\alpha'_1 \alpha'_2 \alpha'_3}}{\partial x} e^{i[(\alpha'_1 - \alpha_1)x + (\alpha'_2 - \alpha_2)y + (\alpha'_3 - \alpha_3)z]} dx dy dz,\end{aligned}$$

the second term in the bracket not contributing anything on account of the orthogonality of the two wave-functions. From the periodicity of the u 's it follows that we may write

$$u_{\alpha_1 \alpha_2 \alpha_3}^* \frac{\partial u_{\alpha'_1 \alpha'_2 \alpha'_3}}{\partial x} = \sum_{n_1, n_2, n_3 = -\infty}^{\infty} A_{n_1, n_2, n_3} e^{2\pi i(n_1 x + n_2 y + n_3 z)},$$

of classical physics by van der Pol and Strutt, "Phil. Mag.," vol. 5, p. 18 (1928). The advantage of the potential field considered in our article as compared with the field $A \cos 2\pi x$ lies in the fact that only elementary functions occur, making the evaluation of the various matrix elements very easy.

[†] O. Haupt, 'Math. Ann.' vol. 79, p. 281 (1919).

[‡] See also Kronig, *loc. cit.*

and introducing this in p_z leads immediately to the conclusion stated above. For two stationary states not separated by a surface of discontinuity of W the matrix element p hence always vanishes.

5. *Applications.*—A problem which we shall investigate here with the help of the one-dimensional model is the reflection of electrons of a given velocity falling from vacuum on to the lattice. The potential will then be as shown in fig. 7, for if our model is to represent an actual lattice, the potential of the

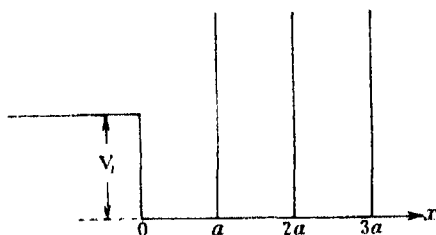


FIG. 7.

bottom of the lattice must be assumed to lie below that outside by a certain amount V_1 . We enquire after a solution representing an incident and a reflected beam of electrons for negative values of x and a transmitted beam for positive values of x . For $x < 0$ we shall have thus :

$$\psi = e^{i\alpha_0 x} + A e^{-i\alpha_0 x}, \quad (14)$$

while for $x > 0$ the solution is given by equation (8). α_0 and β are related by

$$\alpha_0^2 + \kappa^2 V_1 = \beta^2,$$

since the right and left-hand sides of this equation represent respectively the energies of the electron on the left and right of the point $x = 0$, which must be equal. The requirement that the function and its first derivative shall be continuous for $x = 0$ gives us the values of A in equation (14) and of C in equation (8).

AA^* measures the intensity of the reflected beam, that of the incident beam being equal to 1, and is hence equal to the coefficient of reflection R . We find that

$$R = \frac{(\cos \alpha a - \cos \beta a)^2 + (\sin \alpha a - \frac{\alpha_0}{\beta} \sin \beta a)^2}{(\cos \alpha a - \cos \beta a)^2 + (\sin \alpha a + \frac{\alpha_0}{\beta} \sin \beta a)^2} \quad (15)$$

in the allowed regions of βa , while $R = 1$ for the forbidden regions of βa . The

quantity α in equation (15) is the one associated with β in the manner described in the earlier sections. In fig. 8 R is represented as a function of the velocity

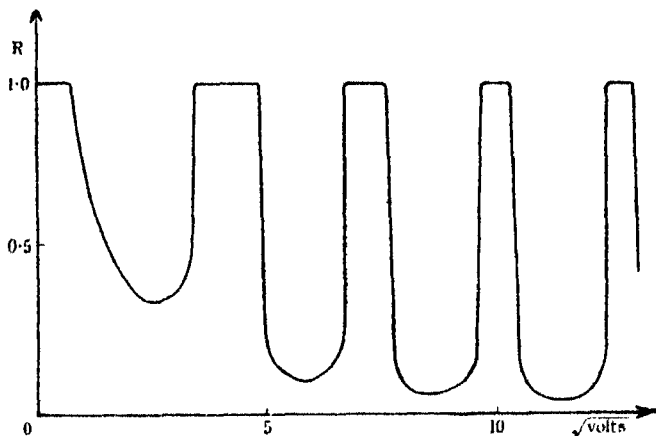


FIG. 8.

of the incident beam measured in $\sqrt{\text{volts}}$, which is proportional to α_0 . For the binding constant P we have again taken $3\pi/2$, while for V_1 and a we have assumed the values $V_1 = 15$ volts, $a = 2.2 \cdot 10^{-8}$ cm. (suggested by the work of Rupp quoted below). The most essential feature of the diagram is, that regions of partial reflection alternate with regions of total reflection, and that these latter have a finite breadth, decreasing as the velocity of the particles gets greater. For very large values of the velocity total reflection takes place only when the lattice constant a is very nearly an integral multiple of the de Broglie wave-length of the incident particles, the regions of total reflection then becoming quite narrow.*

Measurements of the reflection and transmission of electrons in crystal lattices have been performed by various observers.† A quantitative comparison of their results with those obtained here is made difficult by the following circumstances: (1) If we had made our calculation with the three-dimensional

* Morse, 'Phys. Rev.', vol. 35, p. 1310 (1930) has investigated the reflection and scattering of electrons by a crystal in which the potential depends upon the three co-ordinates through terms of the type $A \cos 2ax$. He obtains for the reflection coefficient at perpendicular incidence a curve essentially of the same type as that shown in fig. 8.

† Davison and Germer, 'Phys. Rev.', vol. 30, p. 705 (1927); 'Proc. Nat. Acad.', vol. 14, pp. 317, 619 (1928); Rupp, 'Ann. Physik', vol. 85, p. 981 (1928), vol. 1, p. 801 (1929), vol. 3, p. 497 (1929), and vol. 5, p. 453 (1930); 'Z. Physik', vol. 61, p. 587 (1930); Thomson, 'Proc. Roy. Soc., A', vol. 117, p. 600 (1928), vol. 119, p. 651 (1928), and vol. 125, p. 352 (1929).

lattice, we would have obtained, besides the reflected and transmitted beams, diffracted beams which reduce the intensities of the former; (2) the periodic field of potential considered here differs from that actually present in a metal; (3) in the experiments it is found that some of the incident electrons suffer energy losses due to inelastic collisions with the electrons in the lattice, a phenomenon not provided for in our model. This effect also reduces the intensities of the reflected and transmitted beams. Nevertheless the principal features which appeared in our investigation, viz., the finite breadth of the reflection maxima, the decrease of this breadth with increasing velocity of the incident electrons and the decrease in the ordinates of the reflection minima, can be recognised in the experimental data (see in particular the work of Rupp).

An explanation can be given here also of a phenomenon recently observed by Rupp.* He finds that when the velocity of the incident electrons is gradually increased, new radiations appear in the soft X-ray spectrum of the substance bombarded at about the same velocities at which the reflection coefficient has a maximum. This can be understood if it be remembered that when the velocity begins to exceed that corresponding to the upper limit of a forbidden interval in the energy spectrum of the crystal, the impinging electron can enter into a new region of allowed energy values, giving it new possibilities for radiative transitions. According to this view the excitation threshold should differ from the reflection maximum by an amount equal to half the top-breadth of the maximum (lying toward higher velocities), but since in Rupp's measurements the maxima are already rather sharp the difference is probably obliterated by effects such as the inhomogeneity in the velocities, the imperfections of the crystal, etc. Perhaps, also, the constant energy losses of electrons impinging upon incandescent metals as observed by Rudberg† may be interpreted as corresponding to the transfer of the conduction electrons to the higher allowed regions of energy.

It is hoped to investigate later other physical properties of the model discussed as they appear in the phenomena mentioned at the beginning of this article.

Summary.

1. It is shown that the wave-equation representing the motion of an electron in a periodic field of potential can be integrated in terms of elementary functions when the potential takes the form of a series of equidistant rectangular barriers.

* 'Naturwiss.', vol. 18, p. 880 (1930).

† Rudberg, 'Proc. Roy. Soc.,' A, vol. 127, p. 111 (1930).

When the breadth b of these barriers is made infinitely small and their height V_0 infinitely large, the results become particularly simple, the influence of the barriers depending then only on the product bV_0 .

2. In the one dimensional problem for this limiting case the spectrum of permissible energy values is found to consist of continuous regions separated by finite intervals. By varying the quantity bV_0 from zero to infinity we pass from the case of free to that of bound electrons, and can thus study the changes in the allowed and forbidden ranges of the energy and in the wave-functions during this transition.

3. An investigation of the matrix elements of the linear momentum shows that the electrons can pass through the lattice and that there exists for them the possibility of transition to other stationary states under emission or absorption of radiation, the electrons thus having at the same time the characteristic properties of free and of bound electrons.

4. An investigation of the reflection of electrons by a crystal represented by the field of potential considered leads to results in qualitative agreement with the experimental facts. An explanation of a phenomenon recently observed by Rupp is given, and the possible connection of the theory with measurements of Rudberg is pointed out.

The Hardening of Metals by Rotating Magnetic Fields.

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(Communicated by W. Rosenhain, F.R.S.—Received November 27, 1930.)

In a previous paper* by the author experiments were described in which the hardness of various metals was increased by rotating them in a magnetic field.

It had been observed that metals in a work-hardened condition, and in particular hard steel which had been super-hardened by the "Cloudburst" process† of bombardment with steel balls, exhibit a propensity to become still harder by a process of ageing, the spontaneous increase of hardness commencing with the termination of the work-hardening process, and continuing during a period of several hours or days.

It was assumed that this spontaneous hardening connoted some atomic re-arrangement of an unknown character, and it seemed possible that this re-arrangement might be assisted, in a magnetic metal, by applying an artificial atomic disturbance, such as might be caused by a magnetic polarity of changing direction.

Experiments proved this supposition to be correct. The work-hardened steel was placed across the poles of an electro-magnet and slowly rotated 50 times in one direction and then 50 times in the reverse direction. The result of this magnetic treatment was found to be a distinct increase of hardness.

The electro-magnet used in these original experiments and in those to be described was one which had formed part of an Einthoven string galvanometer. The weight of the magnet is 30 lbs. The gap between the cast-iron pole pieces is one-eighth inch wide. The magnetic flux in a steel specimen placed in contact with the poles and bridging the gap between them is 16,700 gauss. The strength of the open field in the same situation is 1,440 gauss.

The increase of hardness produced by this magnetic treatment having been associated, subjectively, with the spontaneous hardening which had taken place in the work-hardened metal, the question now arose whether there were cases among metals, apart from those which had been work-hardened, where a propensity towards increased hardness or spontaneous hardening by ageing occurred, and whether in these cases also the propensity towards increased

* 'Iron & Steel Inst.,' vol. 120, No. 2 (1929).

† 'Iron & Steel Inst.,' vol. 118, No. 11 (1927).

hardness could be assisted and intensified by the application of a rotating magnetic field.

It was known that in freshly quenched tool steel certain changes take place, accompanied by the evolution of heat over a considerable period of time, and experiments showed that there was also a spontaneous increase of hardness during several hours after quenching. This fact having been established, specimens of tool steel which had been quenched and suitably aged were subjected to the action of the rotating magnetic field, with the result that the hardness was decreased, but almost immediately thereafter an increase of hardness commenced and continued during a period of 3 to 4 hours.

The whole of the effects referred to above are seen in fig. 1, which shows the variations of hardness with time after quenching, magnetic treatment, super-hardening, and repeated magnetic treatment in a high-speed steel containing 0.7 per cent. carbon, 4 per cent. chromium, 1.0 per cent. vanadium, 18 per cent. tungsten, 0.2 per cent. silicon and 0.2 per cent. manganese, and in a specimen of "silver steel" believed to contain 0.8 per cent. carbon and a small percentage of tungsten.

The hardness measurements in the whole of these researches were made originally with the Herbert pendulum hardness tester. This instrument consists of a very short compound pendulum of 4 kg. weight, capable of being balanced on a spherical diamond of 1 mm. diameter. The natural period of oscillation of the pendulum is a measure of the hardness of any material on which it rests, the diamond sphere being the pivot. The "time hardness number" is the number of seconds (taken with a stop watch) occupied by 10 single swings of the pendulum. This number is known to be related in a simple manner to other hardness scales, such as the Brinell, and for the convenience of those not familiar with the time hardness scale it has been converted into approximately equivalent Brinell numbers, the conversion factor in the case of hard steel being 13.5. In the cases of the softer metals, duralumin and brass, referred to later, the original researches conducted with the pendulum were repeated with the Brinell test (5 mm. ball, 125 kg. load, 30 seconds application). The Brinell test gave results entirely similar to those previously obtained with the pendulum, and the actual Brinell readings are given in figs. 5, 6 and 7.

Referring to fig. 1, the specimen of high-speed steel was quenched in oil from 1900° C. Hardness measurements were made immediately after quenching and thereafter at half-hourly intervals, and stability was attained after the lapse of 2 hours. Magnetic treatment was then applied, consisting of 100 slow

revolutions in the magnetic field at 100° C. Previous experiment had shown that the magnetic treatment of hard steel is more effective at 100° C. than at

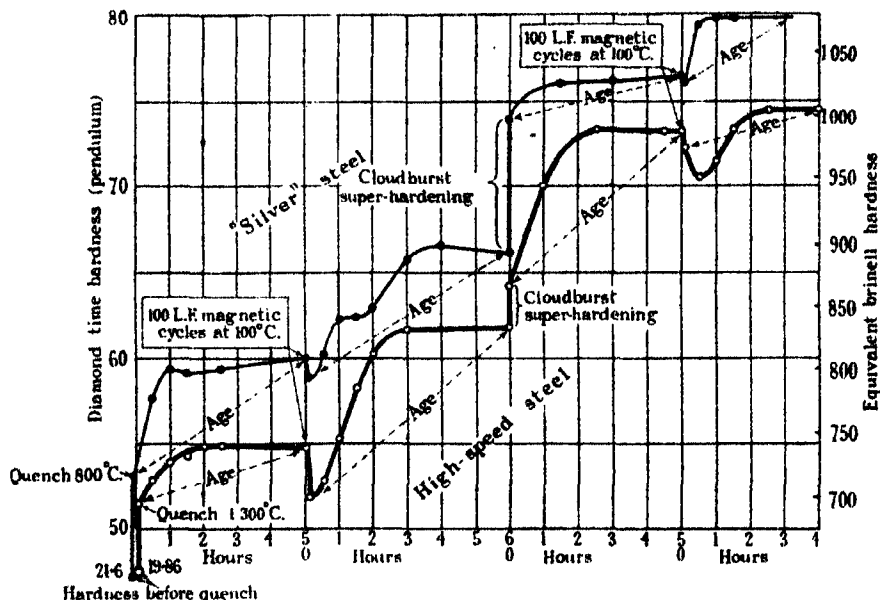


FIG. 1.—Silver Steel and High Speed Steel, Quenched, Aged, Low Frequency Magnetic Treatment, Aged, Superhardened by Cloudburst, Aged, Low Frequency Treatment (second time), and Aged.

room temperature. In treating hard steels a light aluminium vessel was fixed across the magnet poles, and this was filled with water kept at boiling point by a gas burner, the specimen being rotated in the magnetic field (of 14,500 gauss) at the bottom of the water bath.

The result of the magnetic treatment was an immediate decrease of hardness followed by an increase, stability being attained after 3 hours.

The specimen was then treated by the Cloudburst process of bombardment with 3 mm. hard steel balls falling at the rate of 500,000 per minute from heights which were increased by stages from 2 metres to 4 metres. The result of the Cloudburst super-hardening treatment was an immediate increase of hardness and a much more considerable spontaneous hardening during the 2½ hours following the treatment. (It was this age hardening after Cloudburst treatment which first suggested the magnetic hardening process.)

The specimen was then subjected to a second magnetic treatment exactly as before, which again resulted in a decrease and a subsequent increase of hardness.

A precisely similar sequence of hardening operations was applied to the silver steel specimen (fig. 1) and resulted in similar changes of hardness. The total increase of hardness from the moment of quenching was in the high-speed steel from 700 to 1000 Brinell, and in the silver steel from 715 to 1080 Brinell.

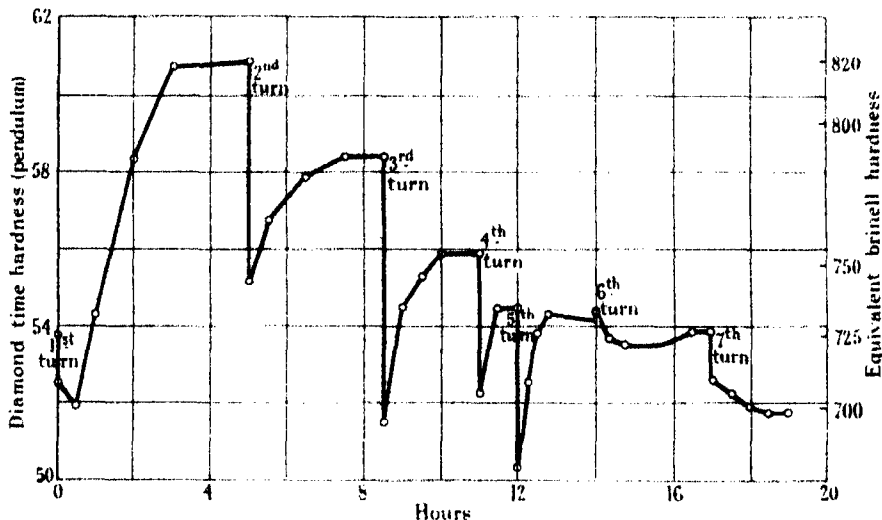


FIG. 2.—High Speed Steel. Effect of Repeated Magnetic Treatment and Ageing.

The effect of repeated magnetic treatment of the same specimen has been the subject of much investigation. The changes of hardness are of a highly complicated character as shown in fig. 2. The specimen used in these experiments was of high-speed steel containing 18 per cent. tungsten. It was cut from a saw blade which had been hardened many months previously by the usual primary and secondary heat treatments at 1300° and 575° C. respectively, and it was assumed to have become stable. The magnetic treatment consisted of a single slow turn in the magnetic field at 100° C., experiment having shown that the effect of a single turn was almost identical in character and degree with that produced by a greater number of turns. The first turn produced an immediate fall of hardness followed by a slight further fall during half an hour and a very pronounced rise during 3 hours. The second turn caused a great fall in hardness followed by a rise to a second and lower maximum, and this sequence of changes was repeated, but with diminishing amplitude, until, after the seventh treatment, there was only a slight decrease of hardness and no subsequent increase.

Fig. 3 shows a similar series of changes resulting from seven successive applications with ageing intervening. The specimen was of steel containing

0.76 carbon, 0.59 manganese, 0.15 silicon, and it was quenched and aged as shown prior to the magnetic treatment. The amplitude of the hardness variations here decreases as before, but a new feature appears in the decrease of

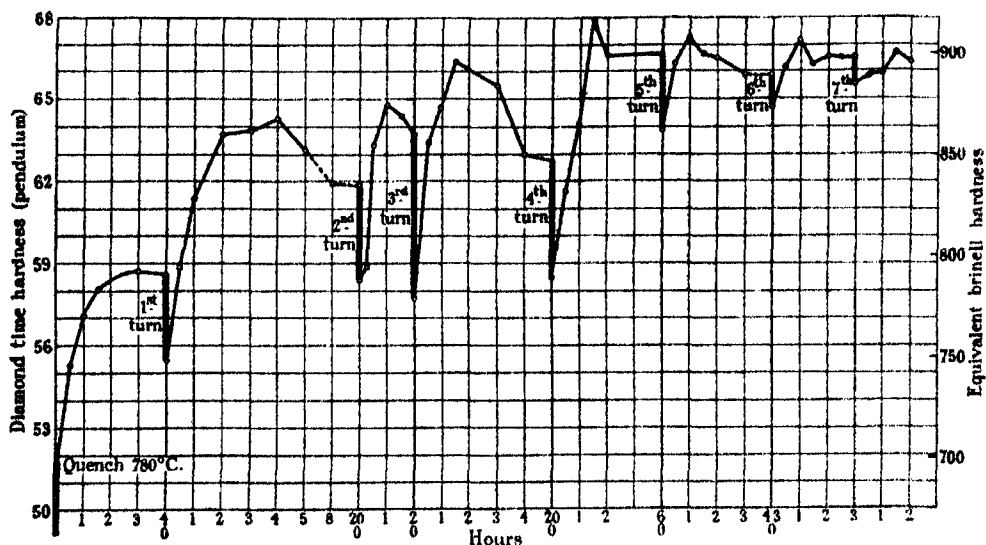


FIG. 3.—Steel (0.76 C., 0.59 Mn, 0.15 Si); Quenched 780° C., Aged, one turn in Magnetic Field at 100° C. repeated seven times.

hardness following the attainment of each maximum, and the general change of hardness is an increasing one.

Fig. 4 shows the result of similar treatment applied to a safety razor blade.

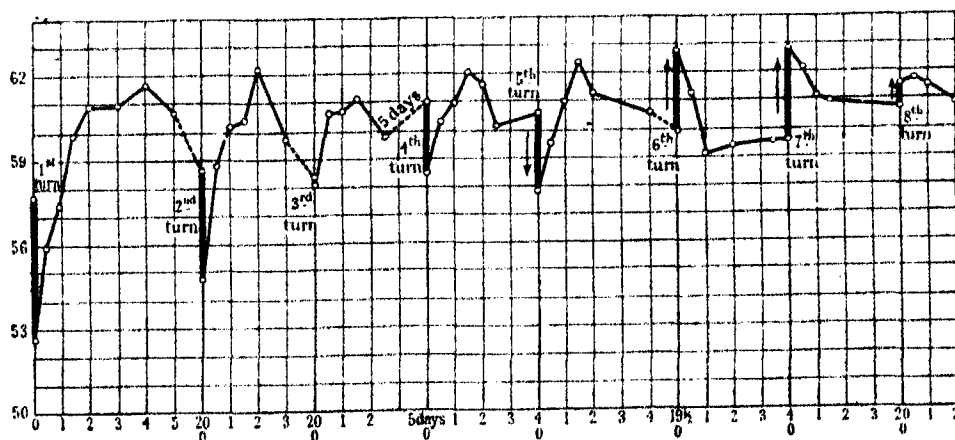


FIG. 4.—Safety Razor Blade. One turn in Magnetic Field at 100° C., repeated eight times.

The results are generally similar, but in the fifth and subsequent cycles there is a curious reversal of the sequence of hardness variations, the previous fall-rise-fall being changed to rise-fall-rise. Significance is attached to this phenomenon because it has been found to recur in other specimens.

Application to Non-ferrous Metals.

The process of age hardening is not confined to ferromagnetic metals, indeed the most notable instance of this process occurs in the non-magnetic* alloy duralumin. Extensive investigations have been made in the application of magnetic treatments to this metal, and as it was at first thought improbable that any effect could be produced in a non-magnetic metal by slowly rotating it in a magnetic field, the first experiments were made (on duralumin freshly quenched from 500° C.) with the high frequency induction furnace, the specimen being immersed in cold water to obviate heating effects. These experiments were followed by others in which the specimen was whirled in the field of the electromagnet by means of an electric motor at speeds from 2000 to 20,000 r.p.m. In every case a notable effect was produced, the general result being a retardation in the initial rate of age hardening followed by an acceleration. Later experiments showed that neither the high frequency field nor the high speed of rotation was necessary, an equally marked effect being produced by slowly rotating the specimen, at room temperature, across the poles of the magnet, or, alternatively, by inserting the specimen for a few seconds between the poles of the magnet, removing it, and reinserting it in a reversed position, the operation being repeated 20 times.

The effect of the last-named procedure is shown in fig. 5. The experiment was first tried on a specimen of duralumin which had been quenched and aged, with the result shown at A. The sequence of hardness changes was a fall-rise-fall, as in the case of the hard carbon steels. When this treatment was applied to a freshly quenched specimen the result, compared with the normal age hardening shown in the dotted curve, was a retardation, a great acceleration (the hardness attained in 12 hours being about equal to that normally attained in 34 hours) and finally a slight fall. The same magnetic treatment applied to this specimen for the second time reproduced the sequence of changes shown at A.

These results suggest that the magnetic effects have been merely superimposed on the normal age hardening process, and may be entirely different

* Later investigation has shown that the specimens of duralumin used in these experiments are diamagnetic. The brass specimens are paramagnetic.

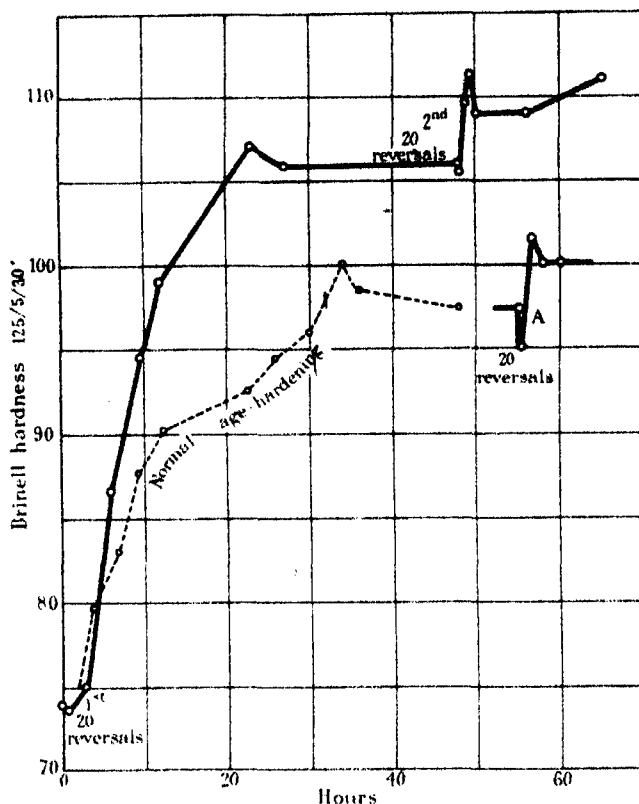


FIG. 5.—Duralumin. Quenched 500° C., Reversed 20 times between Magnetic Poles.

in character. A softening added to a hardening might be expected to result in a retardation, while a hardening added to a hardening would result in an accelerated hardening.

A further example of magnetic treatment applied to freshly quenched duralumin is seen in fig. 6. In this case there was an actual softening, extending over the first 4 hours and followed by accelerated hardening. The treatment, 10 slow turns at room temperature, was applied six times, and in the fourth, fifth and sixth cycles a reversal in the sequence of hardness changes, similar to that which occurred in the razor blade, is seen to have taken place.

Fig. 7 shows the result of applying two different kinds of magnetic treatment to brass. The lower curve refers to cold rolled sheet brass, which was whirled for 5 minutes at 2000 r.p.m. in the magnetic field. The resulting sequence of hardness changes is the same as that found in hard steel and in duralumin, fall-rise-fall, but the cycle of changes was slower, requiring 10½ hours for its

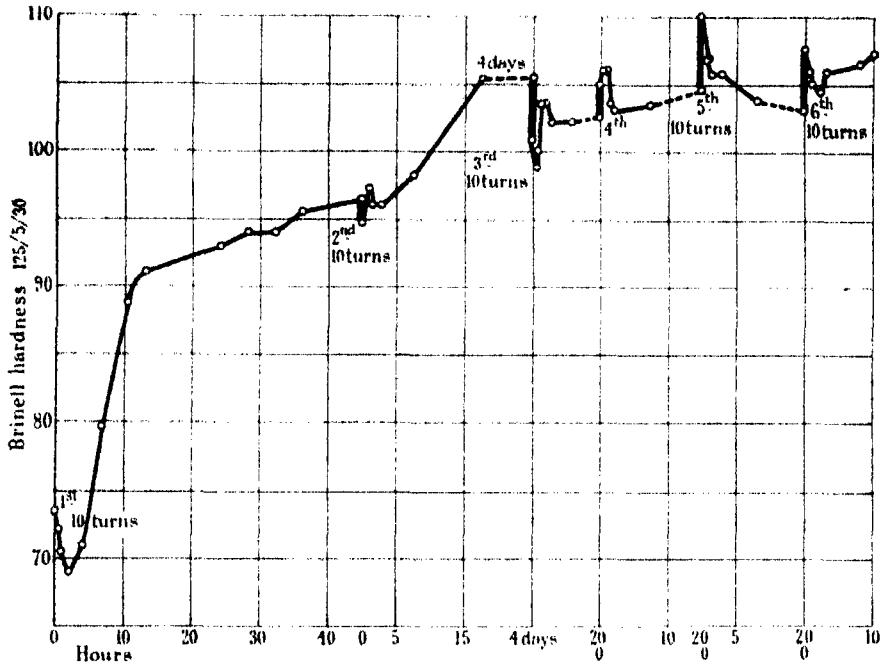


FIG. 6.—Duralumin. Quenched 500° C., 10 slow turns in Magnetic Field repeated six times.

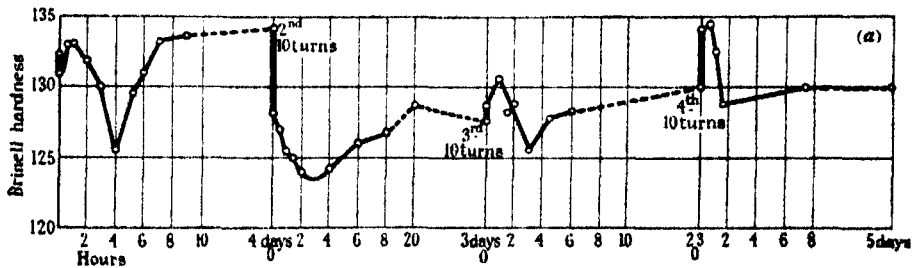


FIG. 7A.—Rod Brass. Ten slow turns in Magnetic Field repeated four times.

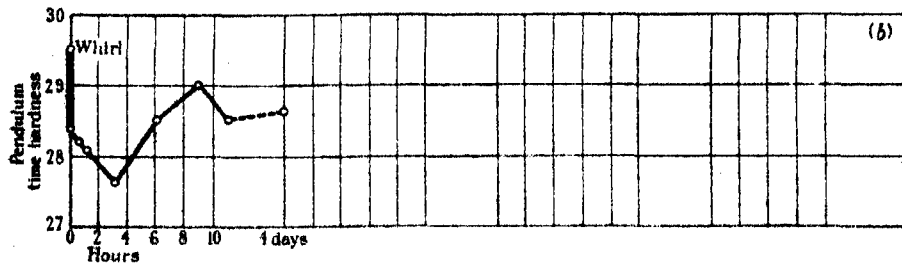


FIG. 7B.—Brass Sheet. Whirled 5 minutes at 200 r.p.m. in Magnetic Field.

completion. In the upper curve fig. 7 are shown the results of slowly rotating a specimen of brass (a disc cut from a bar of commercial rod brass and quenched at 600° C.) across the magnet poles at room temperature. The sequence of changes and their duration are similar to those in the whirled sheet brass, and a reversal in the sequence of changes occurs after the second application, corresponding to the reversals in hard steel, fig. 4, and in duralumin, fig. 6.

The hardness changes here described are believed to indicate a re-arrangement of atoms in the space lattice or a change in the atoms themselves, but no explanation can be given and none will be attempted at the present stage. Some general observations may however be of interest.

The time element enters as an important factor into all the results produced by the rotating field, and it was the discovery of this fact, after a long period of rather fruitless research, which alone rendered possible the presentation of these results. The hardness changes are sometimes very rapid, and in hard steel freshly treated they may be observed from minute to minute.

The hardness induced by magnetic treatment is known to persist for months, and there is no reason to believe that it is other than permanent, though no systematic investigation has yet been carried over long periods of time.

Magnetic treatment has hitherto been applied to various high speed steels and high carbon steels in the hard state, to soft mild steel and soft high carbon steel, to duralumin, and to brass. In every case a series of hardness changes has resulted, the sequence of changes being similar in character. As no metal hitherto subjected to magnetic treatment has failed to react, the possibility must be contemplated that these phenomena are common to all metals. They may not be confined to metallic or even to inorganic substances.

The temperature at which the magnetic treatment is applied has a marked effect on the resulting hardness changes. In the case of hard steel the treatment is less effective at room temperature than at 100° C., but the latter temperature was arbitrarily chosen, and further experiments may show a higher or a lower temperature to be more effective.

In the case of soft steel the magnetic treatment has proved most effective when applied to the cold specimen. An increase of hardness such as would indicate an increase of 20 per cent. in the tensile strength has been induced in soft steel by a single rotation at room temperature, the maximum hardness being attained only after the lapse of 8 hours. The effect of temperature has not yet been investigated in the case of non-magnetic metals.

The practical applications of the magnetic treatment to hard tool steels are obvious. In fig. 2 it will be observed that an equivalent increase of hard-

ness from 725 to 820 Brinell was induced in high speed steel by a single turn in the magnetic field, occupying about 1 minute and applied at a temperature of only 100° C. Such treatment could be given to finished tools of the simplest or the most complicated character, drills, saw blades, milling cutters, dies, or to other articles of steel in which a high degree of hardness is beneficial. The effect of the magnetic treatment on the hot hardness and on the actual cutting efficiency of tools is under investigation. The results obtained on unhardened steels as used in mechanical construction are encouraging and will be further investigated.

In the non-magnetic metals the hardness changes hitherto produced have been relatively slight. The theoretical importance of these phenomena is believed to be great, but much further investigation will be required to ascertain the nature and extent and possible utility of the changes in the physical and mechanical properties of non-magnetic metals, of which the hardness changes are an indication.

The author acknowledges his indebtedness to Dr. Walter Rosenhain for his kindly interest and advice in connection with these investigations, to Prof. F. C. Thompson for permission to use the high frequency induction apparatus at the Manchester University, and to Dr. Hugh O'Neill for valued advice and assistance in connection with the experiments.

The Scattering of Hard Gamma Rays.—Part II.

By L. H. GRAY, B.A., Fellow of Trinity College, Cambridge.

(Communicated by Sir Ernest Rutherford, F.R.S.—Received December 9, 1930.)

§ 1. *Introduction.*

Three papers* have recently appeared describing investigations of the absorption of the very hard γ -rays from thorium C'' in a number of elements, and in each case the conclusion was drawn that the results indicate that these very high energy quanta are capable of interacting with certain atomic nuclei. The three sets of experimental results do not agree in detail, but in each case the trend of the variation of absorption coefficient with atomic number is very different from the Z^3 law characteristic of photoelectric absorption. Moreover, the difference between the absorption coefficients per electron in heavy and light elements, which has hitherto been attributed to photoelectric absorption, is nearly as great for the hard thorium C'' γ -rays ($h\nu = 2.65 \cdot 10^6$ e-volts) as for the much softer radium C γ -rays ($h\nu \sim 1.8 \cdot 10^6$ e-volts), in marked contrast with the rapid variation with wave-length observed in the softer γ -ray region of the spectrum.

Very little is at present known concerning the magnitude of the photoelectric effect in the γ -ray region, and since absorption coefficients measured in the usual manner are the sum of two terms referring respectively to scattering and to photoelectric absorption, it is essential for the further elucidation of the problem to study the actual scattered radiation.

A preliminary investigation by the author† has already been described. When these experiments were undertaken it appeared that the absorption coefficient of the hard thorium C'' γ -rays varied irregularly from element to element in the periodic system, being sometimes approximately equal to the theoretical Klein-Nishina value, and sometimes as much as 12 per cent. greater in a neighbouring element. A careful comparison using radium C γ -rays filtered through 4 cm. of lead revealed no difference as great as 0.5 per cent. in the energy scattered in the forward direction between 16° and 90° by sulphur and aluminium, which appeared to be respectively normal and abnormal

* Tarrant, 'Proc. Roy. Soc.,' A, vol. 128, p. 345 (1930); Meitner and Hupfeld, 'Naturwiss.,' vol. 22, p. 534 (1930); 'Phys. Z.,' vol. 31, p. 947 (1930); Chao, 'Proc. Nat. Acad. Sci.,' vol. 16, p. 431 (1930).

† 'Proc. Roy. Soc.,' A, vol. 128, p. 361 (1930).

elements. Technical difficulties prevented the use of thorium C'' γ -rays and the extension of the comparison to heavy elements. A more complete investigation has now been made of the scattering power of seven elements ranging in atomic number from magnesium to lead, using radium C γ -rays filtered through 4 cm. of lead, and thorium C'' γ -rays filtered through 3 cm. of lead.

It is always assumed that the scattering power of an atom is proportional to the number of the extranuclear electrons. A departure from this rule might arise in two ways :—

- (1) Because the binding forces were not without influence on the scattering power of electrons in heavy atoms.
- (2) Through the interaction of γ -radiation with the nucleus.

While we may not in general be able to investigate these two possibilities independently, we may by a suitable disposition of apparatus, make the experiment specially sensitive to one or other type of abnormality. For, on theoretical grounds, it is unlikely that the nucleus or any of its components will give rise to ordinary Compton scattering. It is much more likely that any interaction with radiation should be of the nature of a resonance phenomenon, analogous to optical fluorescence, involving transitions of positive particles between different energy levels, and resulting in the subsequent emission of γ -radiation of the same hardness as that of the incident radiation. Compton scattering, on the other hand, leads to a secondary emission predominantly in a forward direction. The fluorescent radiation may be distinguished from the small amount of radiation scattered in the backward direction on account of its much greater hardness.

From the account given previously (*loc. cit.*) of the earlier investigations, it will be evident that no accurate data are available for the scattering of hard γ -rays by heavy elements. It seemed desirable, therefore, first to test the validity of the Klein-Nishina formulæ for heavy elements, by comparing the intensity of the radiation scattered in the forward direction by heavy and light elements. This was made possible by the use of an ionisation chamber containing oxygen at 80 atmospheres pressure. The elements compared were magnesium, aluminium, copper, zinc, cadmium, tin and lead, using radium C γ -rays filtered through 4 cm. of lead, and thorium C'' γ -rays filtered through 3 cm. of lead, the latter constituting a practically homogeneous beam of quantum energy, $2.65 \cdot 10^6$ e-volts. Nearly half the total energy scattered by the extranuclear electrons falls within the angular range examined, viz., 10° to 30° , whereas only 6 per cent. of an isotropic radiation would have been

measured. The measurements, therefore, were specially sensitive to differences in the extent of the scattering by the extranuclear electronic system. No variations in the scattering power of different elements have been found—either irregular or systematic—beyond such as might be attributed to experimental error, which was of the order of 1 per cent. We may therefore conclude that the binding forces are without sensible influence on the scattering power of the extranuclear electrons.

In spite of the insensitiveness of the investigation to isotropic radiation we may conclude further that not more than a third of the difference between the directly measured absorption coefficients of the thorium C' γ -rays in lead and water can be due to fluorescence of the type considered. This aspect of the investigation will be considered more fully in § 9. Experiments are now in progress designed specifically to reveal any evidence for the emission of a secondary radiation such as may result from nuclear interaction.

THE SCATTERING OF HARD THORIUM C' GAMMA RAYS.

§ 2. *The Radioactive Source.*

Apart from the very weak γ -rays of potassium the hardest known γ -rays are emitted by thorium C'. The natural β -ray spectrum of this body was studied by Black, who deduced that the γ -ray spectrum consisted of a single strong line of quantum energy, $2.65 \cdot 10^6$ e-volts, and three weaker lines at about half a million volts. It has been estimated by Bastings* that 80 per cent. of the total energy emission is contained in the hard line, but it is almost certain that this figure is too high, for after filtering through 3 cm. of lead, the proportion of softer radiation remaining in the beam would be inappreciable, whereas Chao,† using a steel electroscope, observes an 8 per cent. decrease in the absorption coefficient in lead on increasing the filter thickness from 3 to 7 cm. On the basis of these figures it would appear that after filtering through 3 cm. of lead 7 per cent. of the energy of the beam consisted of the softer radiations. From the standpoint of the present investigation this small admixture of softer radiation would be quite unimportant were it not for the fact that it complicates somewhat the corrections which have to be made for reabsorption. Nevertheless thorium C' provides the closest practical approach to a homogeneous source of hard γ -radiation.

The source used in this investigation consisted of thorium C', equivalent in

* 'Phil. Mag.,' vol. 5, p. 785 (1928).

† 'Proc. Nat. Acad. Sci.,' vol. 16, p. 431 (1930).

activity to about 10 mgm. of radium, in equilibrium with radiothorium. The γ -rays from thorium B were thus present in the primary beam, but being softer than the soft components from thorium C'' would be completely removed by the filter. Remembering that 160 millicuries of radon were used in the aluminium sulphur comparison (*loc. cit.*), it will at once be evident that the experiment involves the measurement of extremely weak radiations. The difficulties were further increased by the fact that the investigation was to extend to heavy as well as light elements. For this purpose, in order that the corrections may be satisfactorily applied, it is necessary to examine only the radiation scattered through a comparatively narrow angular range. The range 10° to 30° was employed in these experiments; it will be seen from fig. 3 that this range includes the peak of the angular distribution curve, and at the same time does not include any scattered radiation of wave-length greater than 9 X.U. In fulfilling these theoretical desiderata, however, the ionisation current due to the scattered radiation has been reduced to about 1 ion per cubic centimetre per second—in fact, of the same order as that due to “penetrating radiation.”

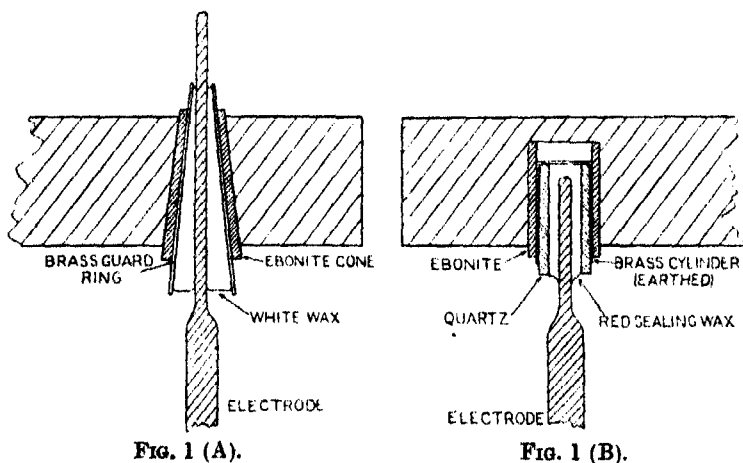
§ 3. *The Ionisation Measurements.*

The accurate measurement of these very weak radiations was made possible by the use of a steel ionisation chamber containing oxygen at 85 atmospheres pressure. The advantages of the increase of pressure are twofold. In the first place, the magnitude of the ionisation current produced in a vessel of a litre capacity by the radiation under investigation is increased to about 10^5 ions per second, thus becoming easily measurable by the Townsend balance method, using a Compton electrometer at a sensitivity of about 2500 divisions per volt. Secondly, owing to the increased effective range in the gas, that part of the natural activity due to β -particles is increased perhaps fiftyfold relative to that due to α -particles, resulting in a very great reduction in the fluctuations which formerly limited the accuracy of measurement. It seems probable that the use of very high pressure still further discriminates in a favourable manner between α -particle and β -particle ionisation, by preventing the attainment of saturation in the former case. By the standard procedure of measuring the ionisation current produced by two sources separately and together, it was found that a field of 40 volts per cm. sufficed to produce practical saturation. On the other hand, the difficulties ordinarily experienced in attaining saturation in the case of ionisation produced by α -particles in air at atmospheric pressure make it certain that the currents must be very far removed from saturation at 100 atmospheres, when the rate of recombination

has been increased by a factor of 10^4 . It would thus appear that the high pressure actually tends to suppress the α -particle ionisation. Indeed, it seems necessary to make such an assumption in order to explain the small natural activity observed; in these experiments in approximate agreement with the measurements of Broxon,* the natural activity at 80 atmospheres pressure was 68 ions per cubic centimetre per second (at that pressure), only about three times that of the brass ionisation chamber used previously at atmospheric pressure.†

The ionisation chamber is shown diagrammatically to scale in fig. 2. The cylindrical walls were turned from steel tubing, and were 0.8 cm. thick. The top and base, which were made from steel blanks 2.5 cm. thick, rested on collars on the inner cylinder, and were pulled down on to the outer cylinder by 12 steel bolts. The choice of a suitable packing, and the insulation of the electrodes presented certain difficulties. It was found eventually‡ that red fibre packing smeared with gold size was entirely satisfactory. No decrease in pressure was detected while the chamber was in use, though as much as 1 per cent. in a week would certainly have been noticed.

The electrode system is shown in detail in fig. 1.



A cylinder of steel gauze, about 5 mm. mesh, was supported by two brass electrodes, only one of which emerged through the top of the chamber. The

* 'Phys. Rev.', vol. 27, p. 542 (1926).

† It is a pleasure to acknowledge my indebtedness to Mr. T. E. Harris, of Denver, Norfolk, for constructing the ionisation chamber in his private workshop.

‡ I wish to acknowledge the assistance of Mr. G. T. P. Tarrant, who collaborated with me in overcoming these technical difficulties.

electrode B, which merely served to support the gauze cylinder, was insulated in the usual manner. It was cemented by red sealing-wax into a short length of quartz tubing, which had been previously cleaned and "fired." The quartz was cemented inside a brass tube, connected by a third electrode (not shown in the figure) to earth. This brass tube was insulated from the steel case by a thin piece of ebonite tubing. The insulation of the electrode A, however, presented difficulties because red sealing-wax had to be abandoned. The power of red sealing-wax to make hermetically tight joints resides in its glazed surface, which always cracked under the great pressures employed. A white wax much used in vacuum technique was found quite satisfactory, both in maintaining the pressure and in its insulating properties. As shown in the figure, the electrode A was set in a conical brass tube, which served as a guard ring, being insulated from the steel top by a conical ebonite tube. It was found essential to grind the various components to the same taper before cementing them together with white wax. The third electrode connected to the guard ring of B was constructed on the same plan, but being at earth potential needed no guard ring.

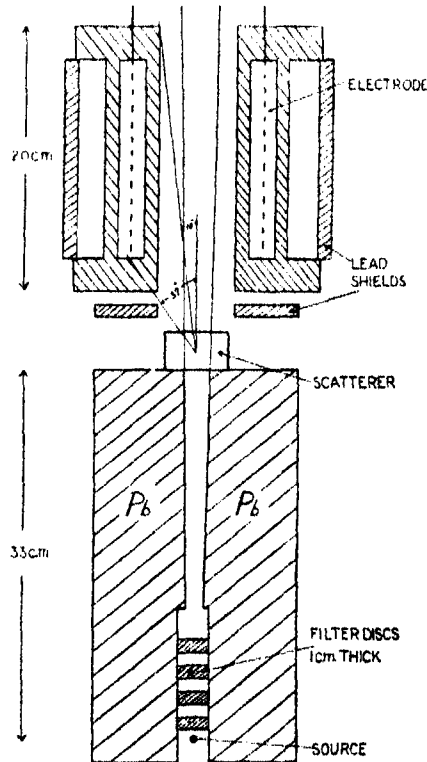


FIG. 2.

The disposition of the ionisation chamber with respect to the canalising system and the scatterer is shown in fig. 2. It differs in certain important respects from that previously used. On account of the greater penetrating power of the thorium C'' γ -rays, the length of the canalising system was increased to 33 cm. The base of the ionisation chamber was raised above the scatterer, which rested on the top of the canalising system, so that only radiation scattered between 10° and 30° was measured. In consequence of these changes it was necessary to reduce the solid angle of the γ -ray beam, and in order to prevent direct rays reaching the chamber by cutting diagonally across the top of the canalising system the central hole was made conical. This gives rise to a very sharply defined beam, as was evident from the image produced on a photographic plate placed immediately above the chamber.

As before, the apparatus was mounted on a light wooden stand, and was set up at least a metre from any other object. In this way it was secured that once scattered radiation from surrounding objects will consist of quanta deflected through at least 160° , and consequently having a wave-length of at least 46 X.U. It would therefore be almost completely absorbed in the lead sheath surrounding the chamber. There was, in fact, as the following table shows, a small amount of ionisation produced by this radiation.

When there was no scatterer in the path of the main beam, the total ionisation comprised the three contributions :—

Natural activity of chamber	68.6 J
Radiation scattered from the walls of the canalising lead blocks	27.4 J
Radiation scattered from the surrounding objects and the walls of the room	20.6 J
Sum	116.6 J

The unit J is a rate of production of 1 ion per cubic centimetre per second at the pressure used in the experiment.

§ 4. *The Scatterers.*

Scatterers of the materials to be investigated, magnesium, aluminium, copper, zinc, cadmium, tin, and lead were constructed in the form of discs 5 cm. in diameter, and thickness inversely as the electron density. Care was exercised to insure that the surfaces were plane, so that the relative number of electrons

per square centimetre in each could afterwards be determined exactly by weighing, and measuring the diameter. Each scatterer was mounted in a thin brass disc, so that their centres should be at the same distance below the ionisation chamber, thus avoiding large corrections (6 per cent. per cm.) for the difference in angular range of scattered radiation that would have been investigated. Small corrections were applied for the slight differences existing in the superficial electron density of the scatterers and the positions of their centres, as indicated in Tables III and IV.

§ 5. *Experimental Procedure.*

Besides making the measurement of each current a symmetrical operation it was further necessary to extend the symmetry so as to take account of long period changes. For, as previously mentioned, the ionisation produced by the scattered radiation under investigation was of the same order as that produced by "penetrating radiation." It appears that even at sea level this ionisation may vary by as much as 2 per cent. in 6 hours. Apart from these possible variations following sidereal time, there are certainly variations depending on local conditions, such as the barometric pressure, which cannot be eliminated except by establishing correlation coefficients based on the statistical analysis of a great many measurements.

On the assumption that the latter type of variation tends to consist of a uniform change throughout the day, its effects can be diminished by the symmetrical arrangement of the measurements. Three elements were examined each day, of which magnesium was always one. They would be examined, *e.g.*, in the order, magnesium, aluminium, zinc, zinc, aluminium, magnesium. Magnesium was included in each day's measurements so that any change in pressure of the gas in the chamber could be detected and eliminated. As the measurement shows no certain change with time, a simple mean was taken for each element. A second complete set of observations was taken. In order to minimise the influence of the first type of variation, following sidereal time (and therefore, during the period of the measurements, the same from day to day), the elements were examined in the same groups, but the order within the group was changed. This will be clear from Table I. The departure from this system on July 14, 1930, was accidental.

Certain subsidiary measurements which were required in order to apply the necessary corrections are recorded below (Table II). The source was removed for the determination of the natural activity of the chamber. Measurements were made with the magnesium and lead scatterers in position to make

Table I.

Time.	Mag- nesium.	Alumi- nium.	Copper.	Zinc.	Cad- mium.	Tin.	Lead.
July 9, 1930—							
10.32	1·644	—	—	—	—	—	—
12.03	—	1·653	—	—	—	—	—
1.32	—	—	—	1·635	—	—	—
3.02	—	—	—	1·646	—	—	—
4.26	—	1·654	—	—	—	—	—
5.50	1·633	—	—	—	—	—	—
July 10, 1930—							
10.15	1·642	—	—	—	—	—	—
11.40	—	—	—	—	—	1·627	—
1.05	—	—	—	—	—	—	1·608
2.30	—	—	—	—	—	—	1·602
3.54	—	—	—	—	—	1·620	—
5.17	1·636	—	—	—	—	—	—
July 11, 1930—							
10.18	1·630	—	—	—	—	—	—
12.08	—	—	1·637	—	—	—	—
1.25	—	—	—	—	1·627	—	—
3.0	—	—	—	—	1·663*	—	—
4.22	—	—	1·630	—	—	—	—
5.44	1·640	—	—	—	—	—	—
July 14, 1930—							
10.02	—	1·624	—	—	—	—	—
11.26	1·646	—	—	—	—	—	—
12.51	—	1·634	—	—	—	—	—
2.44	—	1·635	—	—	—	—	—
4.08	—	—	—	1·632	—	—	—
5.10	—	—	—	1·629	—	—	—
July 15, 1930—							
10.05	—	—	—	—	—	1·622	—
11.30	—	—	—	—	—	—	1·567
12.53	1·636	—	—	—	—	—	—
2.20	1·644	—	—	—	—	—	—
3.50	—	—	—	—	—	—	1·580
5.20	—	—	—	—	—	1·604	—
July 16, 1930—							
10.04	1·623	—	—	—	—	—	—
11.34	—	—	—	—	1·631	—	—
1.0	—	—	1·642	—	—	—	—
2.23	—	—	1·629	—	—	—	—
3.46	—	—	—	—	1·628	—	—
5.09	1·630	—	—	—	—	—	—
Mean values	1·639	1·640	1·634 _s	1·635 _s	1·629	1·618	1·589

Probable error of each mean value = 0·25 per cent. or 0·004 . 10⁵ ions per second.

* This observation was discarded in taking the mean since it differed from the mean by more than eight times the probable error, but was taken into consideration in evaluating the probable error.

The unit of current adopted in the above table is 10⁵ ions per second or roughly 100 ions per cubic centimetre per second.

sure that no large change in the natural activity was caused by the presence of these scatterers, either by absorbing radiation coming from the lead canalising system in the former case, or by the possible activity of the scatterer in the latter. No such difference was observed, but the accuracy of these measurements was considerably less than those of Table I. Had the latter hinted at any irregularity arising in the way suggested, a more accurate investigation would have been made.

Table II.

Natural activity---

No scatterer	0.691 . 10 ⁵ ions per second.
Magnesium	0.702
Magnesium	0.631
Lead	0.703
No scatterer	0.704
Mean	<u>0.686 . 10⁵</u>

Measurements made on July 12, 1930, between the two sets of observations recorded in Table I. Source in position (undisturbed) :—

No scatterer	1.161 . 10 ⁵ ions per second.
	1.171
Mean	<u>1.166 . 10⁵</u>

Lead plug filling conical hole to absorb canal radiation	0.894 . 10 ⁵ ions per second.
	0.890
Mean	<u>0.892 . 10⁵</u>

Whence---

Radiation scattered from canal walls.....	0.274 . 10 ⁵ or 27.4 J
Radiation scattered from walls of the room	0.206 . 10 ⁵ or 20.6 J
Natural activity	0.686 . 10 ⁵ or 68.6 J

§ 6. Corrections.

The major corrections fall into three classes : (1) correction for the absorption of the direct beam ; (2) for the partial reabsorption of the scattered radiation ; and (3) for the absorption of the radiation scattered from the walls of the canal. In applying these corrections the same procedure has been adopted as formerly in the aluminium sulphur comparison.* The absorption data used throughout are based on the Klein-Nishina scattering formulæ and the empirical photo-electric law :—

$$\log_{10} \tau = 3.6505 + 1.0 \log_{10} \lambda + 0.480 (\log_{10} \lambda)^2.$$

At 100 X.U. the law becomes identical with the X-ray photo-electric law, but it only accounts for part of the difference between the absorption coefficients

* *Loc. cit.*

of the thorium C'' γ -rays in heavy and light elements. It seems necessary to postulate the existence of an additional absorbing mechanism which is only operative in the case of very hard γ -rays. The assumption has been made (and is consistent with experiment) that the absorption curve exhibits a discontinuity immediately on the long wave-length side of the thorium C'' line.

This law was chosen after a consideration of the available experimental data, and will be discussed in detail elsewhere.

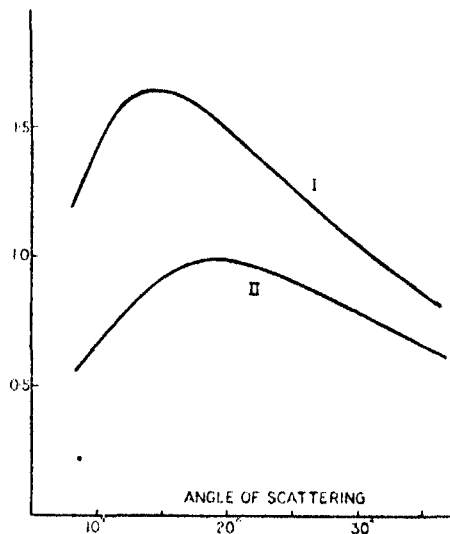


FIG. 3.

The intensity of radiation scattered between θ and $\theta + d\theta$ at various angles is shown in fig. 3. Curve I for the wave-length 4.7 X.U. This radiation is absorbed to varying degrees in passing (at large angle of incidence) through the inner steel wall of the ionisation chamber. The resultant ionisation at each angle is given by Curve II. The three corrections mentioned above have been estimated graphically for each element, using this curve as a basis.

The corrections appropriate to scatterers having exactly the same superficial electron density (the aluminium scatterer was used as standard) are tabulated in the first three columns of Table III. The fourth column shows the sum of these corrections appropriate to the actual scatterers. The next two columns contain the corrections for the inequalities in the superficial electron densities of the scatterers, and in their positions relative to the chamber. Finally these corrections are added to the observed ionisation due to the scattered radiation taken from Tables I and II and expressed in the last column as a percentage of the scattering power of magnesium.

Table III.

	Absorption of direct beam.	Absorption of scattered radiation.	Absorption of canal radiation.	Sum appropriate to actual scatterers.	Correction for thickness.	Correction for position.	Total correction.	Ionisation due to scattered radiation (corrected).	Relative scattering power per electron.
Magnesium	5.6	7.0	5.7	18.3	—	—	18.3	65.6	100.0
Aluminium	5.7	7.0	5.7	18.4	0.4	—0.1	18.6	66.0	100.5
Copper	5.8	7.5	6.0	19.1	0.9 ₅	—	20.0	66.8 ₅	101.8
Zinc	5.9	7.5 ₅	6.0	19.3	0.8	—	20.1	67.0 ₅	102.1
Cadmium	6.3 ₅	8.1	6.4	20.5 ₅	0.8	0.4	21.7	68.0	103.6
Tin	6.4	8.2	6.4	20.6 ₅	1.1	—	21.7 ₅	68.9 ₅	101.9
Lead	7.7	10.0	7.4	25.2	—0.3	—	24.9	67.2	102.4

Currents are expressed in ions per cubic centimetre per second.
 Probable statistical error of figures in the last column = 0.6 per cent.

§ 7. *The Probable Limits of Error.*

It is clear in the first place that, having regard to the probable error of the measurements, there is no certain evidence of any irregular variation of the electronic scattering power with atomic number.

Taking into consideration the fact that, owing to the greater number of measurements made, the probable error in the case of magnesium is only half that in the other elements, the figures in the last column undoubtedly show a general upward tendency, amounting to a difference of about 1 per cent. as between magnesium and lead. This difference cannot be attributed to ionisation produced by fluorescent radiation from the heavy elements. The relative probability of photoelectric absorption and scattering, the angular distribution of these radiations, absorption in the scatterer itself, and in the steel wall of the ionisation chamber, are all factors favouring the measurement of the scattered radiation, which rough calculation indicates must be greater than the fluorescent radiation by at least the factor of 1500.

It is possible that the progressive increase from magnesium to lead is attributable to a faulty estimation of the corrections. The uncertainty arising from these corrections is not as large as at first sight it might appear. Thus the fact that all the scatterers were of equivalent thickness at once limits the possibility of serious error to the differences between heavy and light elements—a difference estimated at 10 per cent. Moreover, part of this difference is due to the absorption of the main beam, for which the correction is based on the direct experimental observations of Chao. This reduces the difference with which we are concerned to 6·5 per cent., but nevertheless, considering the rather tentative nature of the photoelectric law that has been used, leaves ample room for the introduction of a 1 per cent. error.

A PARALLEL INVESTIGATION USING STRONGLY FILTERED RADIUM C GAMMA RAYS.

§ 8. *Experimental Procedure and Results.*

A parallel investigation, using radium C γ -rays filtered through 4 cm. of lead was carried out in the manner described for thorium C'', except that only one complete set of measurements was made. A very much stronger source (radon) was used, resulting in a tenfold increase in the ionisation currents. In consequence, the secular changes in natural activity were relatively unimportant. The experimental results and the corrections are presented in Table IV. The

Table IV.

	Absorption of direct beam.	Absorption of scattered radiation.	Absorption of canal radiation.	Sum appropriate to actual scatterers.	Correction for thickness.	Correction for position.	Total correction.	Ionisation due to scattered radiation (corrected).	Relative scattering power per electron.
Magnesium	164	186	161	512	—	—	512	1646	100.0
Aluminium	164	186	161	509	9	—4	514	1654	100.5
Copper	167	188	162	511	22	—	533	1636	99.4
Zinc	167	188	162	512	19	—	531	1677	101.9
Cadmium	175	194	168	531	19	—	550	1647	100.0
Tin	177	196	169	533	26	—	559	1618	98.3
Lead	224	226	195	647	—5	—	642	1602	97.6

Probable statistical error of figures in the last column = 0.3 per cent.

currents recorded refer to the ionisation per cubic centimetre per second, after subtracting the natural activity and correcting for the decay of the source.

These results, as well as those previously obtained for the scattering of the thorium C'' γ -rays are represented graphically in fig. 4. As in the former case, the mean departure of these points from the smooth curve is only a little greater than the probable statistical error of the measurements. At first sight there might appear to be some evidence of a correlation between the irregularities in the two sets of measurements, but in view of the assigned probable error the agreement must at present be regarded as fortuitous.

There is again a progressive change from magnesium to lead. The possibility that it is due to the faulty application of the necessary corrections cannot be ruled out, even though the curves tend in opposite directions, since it was assumed that the photoelectric absorption changes more or less abruptly on the long wave-length side of the thorium C'' line. The measurements nevertheless make it reasonably certain that the scattering coefficient in lead does not differ from that in light elements by more than a few per cent.

The two experiments together embrace about an octave—from 4.7 to 10 X.U., and on account of the particular experimental disposition employed, the measurements were specially sensitive to differences in the extent of the scattering by the extranuclear electronic system. No variations have been found—either irregular or systematic—beyond such as might be attributed to experimental error, which was of the order of 1 per cent.

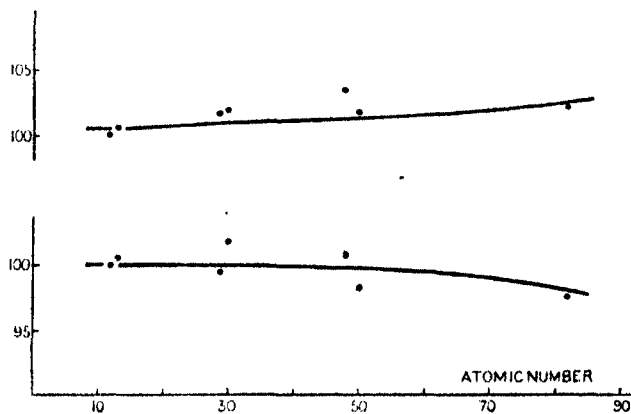


FIG. 4.—Relative Scattering Power. Atomic Number.

Thorium C'' Gamma Rays (3 cm. lead filter).

Radium C Gamma Rays (4 cm. lead filter).

THE EXPERIMENTAL RESULTS CONSIDERED IN RELATION TO THE POSSIBLE INTERACTION OF THE THORIUM C'' GAMMA RAYS WITH THE NUCLEUS.

§ 9. Considered alone, these measurements provide no evidence of any interaction between hard γ -rays and the nucleus. It is of interest, however, to view them from a different standpoint. What limits do they set to the extent of nuclear scattering, *e.g.*, as considered theoretically by Beck,* and, in particular, how far is it possible to account for the difference in the absorption coefficients of the hard thorium C'' γ -rays in light and heavy elements observed by Tarrant, Meitner and Hupfeld, and Chao, on the hypothesis of nuclear interaction leading to re-emission of quantum radiation?

This latter difference is roughly 80 per cent. of the true scattering coefficient. Clearly therefore it is not due, to any appreciable extent, to the absorption and re-emission of radiation having an angular distribution resembling that of the radiation scattered by the extranuclear electrons. It happens, however, that the apparatus was specially sensitive to the ordinary scattered radiation, for 40 per cent. of this radiation falls within the angular range 10° to 30° , in marked contrast with the corresponding figure 6 per cent. for radiation re-emitted equally in all directions. Nevertheless, even allowing a possible experimental error of 2 per cent. in the relative values of the scattering coefficients of magnesium and lead, not more than a third of the difference in the directly measured absorption coefficients (per electron) in these two elements can be due to any phenomenon resulting in the emission of an isotropic radiation.

Mr. Beck has kindly pointed out to me that if the component of the nucleus set in resonance behaves as an electric dipole, the angular distribution of the fluorescent radiation will be given by the Thomson formula

$$I \propto 1 + \cos^2 \theta.$$

In this case rather more than 8 per cent. of the energy is emitted in the forward direction between 10° and 30° , as compared with 40 per cent. in the case of Compton radiation.

Beck derives an expression for the scattering coefficient S_2 of a single α -particle in the nucleus.

The total absorption coefficient per electron of any element is given by

$$\mu_e = S_1 + \frac{N_a^2}{N_e} \cdot S_2.$$

* 'Naturwiss.,' vol. 18, p. 895 (1930).

where N_a is the number of α -particles set in resonance, and N_e the number of extranuclear electrons per atom.

Since S_1 the ordinary scattering coefficient is equal to $\sigma_e + \sigma_a$, we have

$$\mu_e = \sigma_e + \sigma_a + \frac{N_a^2}{N_e} \cdot S_2.$$

In the case of the thorium C'' γ -rays the observed difference in the energy re-emitted within the range 10° to 30° by lead and magnesium was 2 per cent. Admitting a possible experimental error of 2 per cent., and allowing for the fivefold greater sensitivity to Compton radiation, it follows that

$$\frac{N_a^2}{N_e} S_2 \gtrsim 0.2; \quad \sigma_e \gtrsim 0.008 S_1.$$

If all the α -particles in the lead nucleus are excited, $N_a^2/N_e = 33$, so that

$$S_2 \gtrsim \frac{S_1}{400}, \text{ whereas Beck estimates } S_2 = S_1/100.$$

Thus it would seem either that at most half the α -particles are taking part in the resonance, or that the energy re-emitted by a single particle is only about a quarter of that estimated. Unless the internal absorption coefficient is abnormally large, no appreciable proportion of the radiation re-emitted will be absorbed by the extranuclear electronic system.

The scattering power of lead for the hard radium C γ -rays was found experimentally to be slightly less than that of magnesium (*cf.* fig. 4, p. 538). While this was quite likely due to an inaccurate correction for reabsorption, it will be observed that the difference is in a sense to be expected if the binding forces in lead exert an appreciable influence on the scattering. This would tend to conceal the existence of a fluorescent radiation. Since, however, the intensity of the fluorescent radiation will decrease rapidly with increasing wave-length, and its existence is doubtful even in the case of the thorium C'' γ -rays, it is certainly negligible with radium C γ -rays, so that the influence of the binding forces in this case is at most 1 or 2 per cent. It will be considerably less for the harder thorium C'' radiation, and therefore does not appreciably affect the above considerations regarding the possible extent of the interaction between γ -rays and the nucleus.

It is a pleasure to express my thanks to Sir Ernest Rutherford and to Dr. J. Chadwick for the interest they have taken in this work, and to acknowledge the assistance of Mr. Crowe, who prepared the radon sources.

Summary.

The relative scattering power of the elements magnesium, aluminium, copper, zinc, cadmium, tin, and lead for radium C γ -rays filtered through 4 cm. of lead, and thorium C'' γ -rays filtered through 3 cm. of lead, was investigated by observing the ionisation produced by radiation scattered within the angular range 10° to 30° . In the former case the scattering power of the elements per extranuclear electron appeared to show a slight decrease amounting to 2 per cent. between magnesium and lead, and in the latter case there was a gradual increase of about the same amount; but in each case the difference was of the order of magnitude of the error which might have arisen through uncertainty in the application of the correction for reabsorption of the scattered radiation in the scatterer itself. These measurements therefore establish the fact that the binding forces in heavy elements do not appreciably influence the scattering power of the extranuclear electrons for radiation of quantum energy $h\nu \sim 2 \cdot 10^6$ e-volts.

Since 40 per cent. of the Compton radiation falls within the angular range 10° to 30° the measurements were relatively insensitive to any radiation that might be scattered by the nucleus. It nevertheless seems certain that not more than a third of the difference between the absorption coefficients of the thorium C'' γ -rays in heavy and light elements can be due to nuclear absorption resulting in the re-emission of approximately isotropic radiation.

Flame Speeds in the "Inflammation" and "Detonation" of Moist Carbonic Oxide-Oxygen Mixtures.

By WILLIAM A. BONE, D.Sc., F.R.S., and REGINALD P. FRASER, A.R.C.S.,
D.I.C. -

(Received November 13, 1930.)

[PLATE 8.]

Seeing that hitherto our knowledge of the flame speeds involved in the "inflammation" and "detonation" of carbonic oxide-oxygen mixtures has been mainly confined to those of the theoretical $2\text{CO} + \text{O}_2$ mixture, and that complete data over the whole "explosion range" are needed for the determination of questions relating to the combustion of carbonic oxide, we have lately carried out experiments with a view to supplying the deficiency; and this paper embodies the results thereof.

EXPERIMENTAL.

A.—*Flame Speeds in the Initial Phase of "Inflammation."*

It may be recalled that when a quiescent explosive mixture is ignited at the open end of a horizontal tube, the other end being closed, a slow and usually uniform flame movement is initially set up. Except in mixtures very near to one or other of the explosion limits, this initial phase is soon succeeded by an oscillatory movement during which the flame swings backwards and forwards, usually with increasing amplitude, until it is either extinguished, by swinging too far backwards into its own products of combustion, or gives rise to a much accelerated movement, may be ending up in "detonation" if sufficiently accelerated during a forward swing.

Speaking generally, the initial speed of "inflammation" varies according as propagation is horizontal or vertical, and if the latter then according as it is upwards or downwards. In many cases also it varies with the diameter of the tube; but under defined conditions it is usually uniform and constant, although in one of our previous papers it has been shown that this is by no means necessarily or always so, especially with very sensitive oxygen mixtures.*

In the experiments recorded herein, measurements were made of the initial

* 'Proc. Roy. Soc.,' A, vol. 114, pp. 402 to 419 (1927); see also pp. 103 to 134 of Bone and Townsend's "Flame and Combustion in Gases" for a fuller discussion of the subject.

speeds of inflammation of moist (*i.e.*, "saturated") carbonic oxide-oxygen mixtures when ignited at room temperature (12° to 13° C.) and barometric pressure at the open end of a horizontal glass tube 2.5 cm. internal diameter and 126 cm. long, the other end being closed by a rubber bung.

The two methods, electrical and photographic, described in our previous paper (*q.v.*)* were employed, ignition being effected by gently applying a 2 cm. high coal-gas flame to the quiescent explosive medium. The experimental mixtures had been accurately made up in gas-holders over mercury from carbonic oxide and oxygen, both of a high degree of purity, and the composition of each mixture was checked by analysis, the amount of adventitious nitrogen present never exceeding 0.5 per cent. The amount of water vapour present in each mixture when fired would be about 1.5 per cent.

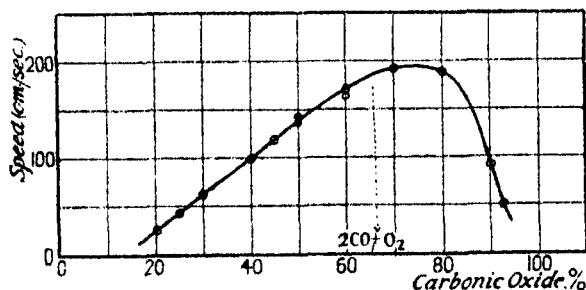


FIG. 1.—Initial Flame Speed in Moist CO—O₂ Mixtures.

The results, which are shown graphically in the speed-composition curve of fig. 1, were as follows :—

Percentage CO in mixture	15	20	25	30	40		
Speed, cm. per second	did not fire	25.2	43.5	60.2	97.5		
Percentage CO in mixture	45	50	60	80	90	92.5	
Speed, cm. per second	119	$\left\{ \begin{matrix} 147.2 \\ 144.0 \end{matrix} \right\}$	$\left\{ \begin{matrix} 167 \\ 163 \end{matrix} \right\}$	177	$\left\{ \begin{matrix} 195 \\ 190 \end{matrix} \right\}$	90.5	$\left\{ \begin{matrix} 51 \\ 51 \end{matrix} \right\}$

It will be seen (i) that the "lower limit" mixture for inflammation is one containing somewhere between 15 and 20 per cent. of carbonic oxide, the explosion range at atmospheric pressure and temperature extending from thence right up to one containing rather more than 92.5 per cent. thereof ;†

* *Loc. cit.*, pp. 405 to 410.

† Le Chatelier found the "limits of inflammation" of moist CO-oxygen mixtures to be between 15.4 and 94.1 per cent. CO-contents, and our present results seem to confirm his.

and (ii) that the mixture giving the maximum initial speed of inflammation would be one containing rather less than 80 per cent. of carbonic oxide.

Comparing these results with those similarly obtained by us for hydrogen and oxygen mixtures at atmospheric pressure, we find that the "explosion range" included all those containing between 10 and about 94 per cent. of hydrogen, with a maximum initial flame-speed at round about 65 to 70 per cent. of hydrogen.*

Moreover, on further comparing them (a) with the results of similar determinations previously made by us in glass tubes of 2.5 cm. internal diameter with moist carbonic oxide-"argon-air"; and moist carbonic oxide-"helium-air" mixtures, respectively, at 17° C. and atmospheric pressure, as well as (b) with similar results for moist carbonic oxide-"nitrogen-air"† mixtures in glass tubes of 2.5 cm. internal diameter at 12° C. and 750 mm. published by W. Payman from the Safety in Mines Research Laboratories‡—the relative data for which are plotted for comparison in the speed-composition-curves shown in fig. 2—we find that all agree in showing (i) the maximum speed-mixture to be one containing a considerable excess of carbonic oxide, over and above the theoretical $2\text{CO} + \text{O}_2 + 3.8\text{R}$ (where $\text{R} = \text{Ar, He or N}_2$) proportion,

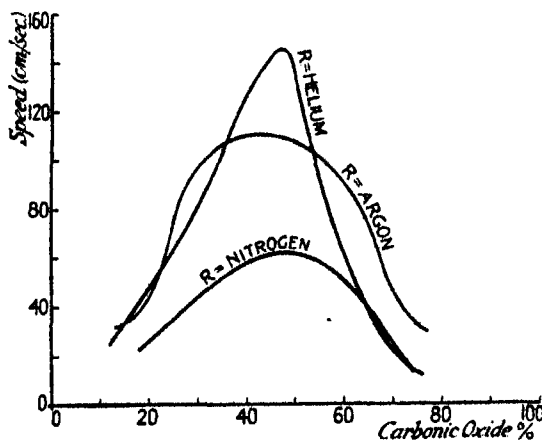


FIG. 2.—Initial Flame Speed in Moist $x\text{CO} + (100 - x)(\text{O}_2 + 3.8\text{R})$ Mixtures.

* *Loc. cit.*, p. 413. Le Chatelier "limits" for hydrogen-oxygen mixtures were at 9.4 and 91.0 per cent. hydrogen, respectively.

† By such expressions is meant an air containing $\text{O}_2 + 3.8\text{R}$, where $\text{R} = \text{Ar, He, and N}_2$, respectively.

‡ 'Trans. Chem. Soc.', vol. 115, p. 1455 (1919). The maximum flame speed was obtained with mixtures containing between 45 and 50 per cent. of carbonic oxide, the CO/O_2 ratio of which would be between 3.9 and 4.8 instead of the theoretical 2.0.

namely, *circa* $3.5 \text{ CO} + \text{O}_2$, $4\text{CO} + \text{O}_2 + 3.8\text{Ar}$, $5\text{CO} + \text{O}_2 + 3.8\text{He}$ and $4\text{CO} + \text{O}_2 + 3.8\text{N}_2$, respectively, and (ii) that whereas excess of CO up to the limit referred to in each case, increased the initial flame speed, excess of oxygen invariably diminished it.

B.—*Flame Speeds in "Detonation."*

Although the late H. B. Dixon* investigated the influence of varying proportions of steam upon the rate of detonation of the theoretical $2\text{CO} + \text{O}_2$ mixtures, and fully dealt with the matter in his Bakerian Lecture of 1893, he did not explore the rates over the whole "detonation range" of carbonic oxide-oxygen mixtures, and little or nothing is known concerning them.

The only information we can find in recent literature is contained in a paper published by R. Wendland† six years ago, a perusal of which leaves us in doubt whether, except in perhaps one or two experiments, he had succeeded in establishing a true "detonation" in his mixtures. For his observed rates are generally too low, and seem rather to pertain to what is now known as the "pre-detonation" phase, which indeed may easily be mistaken for the real thing. Also we think that his explosion tube (only 5 metres long) was too short, and his method of initiating detonation in his experimental mixture uncertain.

According to him, the lower limit of detonation of moist carbonic-oxide-oxygen mixtures at 18° and atmospheric pressure lies between 38 and 39 per cent. carbonic oxide content, where the speed was found to be 1340 metres per second in a 2.1 cm. diameter tube, which seems rather low for a true detonation. For a mixture containing 50.7 per cent. of carbonic oxide he found a speed of 1610 metres per second, which again seems low. The only speed recorded in his paper which we think undoubtedly relates to true detonation is 1740 metres per second for a mixture containing 65.6 per cent. of carbonic oxide. Thus H. B. Dixon found 1703 metres per second for a moist $2\text{CO} + \text{O}_2$ (saturated at 20°C.) mixture, and we have found 1750 metres per second for a moist (saturated at 18°C.) mixture containing 67 per cent. of carbonic oxide.

It has been abundantly proved, in the course of recent work in both the late H. B. Dixon's laboratory and our own, that with moist carbonic oxide oxygen mixtures not only may the somewhat lower speeds involved in the "pre-detonation period" be easily mistaken for those of true detonation,

* 'Phil. Trans.,' vol. 184, pp. 97 to 188 (1893).

† 'Z. Phys. Chem.,' vol. 110, p. 637 (1924).

but that when first established the speed of the "detonation" may be much higher for a while than the true constant speed eventually attained, particularly if and when the flame is overtaking a series of shock waves at the instant when detonation is set up. Thus, for example, in the course of our previous experiments, speeds up to 1575 metres per second were observed during the pre-detonation stage of a moist (saturated at 15° C.) $2\text{CO} + \text{O}_2$ mixture in a tube of 1.25 to 1.3 cm. internal diameter; and in circumstances where detonation was set up under the influence of successive "shock waves," and just as the flame was overtaking one of them, speeds (in each case apparently constant for a time) of anything between 1,900 and 2,170 metres per second were observed.* The true speed of detonation for the mixture, uncomplicated by the circumstances referred to, would be rather less than 1750 metres per second in a tube of said internal diameter.

According to our experience, in order to be sure of measuring the true speed of detonation of a moist carbonic-oxide-oxygen mixture it is necessary (i) to arrange the firing so that detonation is established with certainty as soon as possible in the medium without the interference of extraneous "shock waves," and (ii) to show that the speed measured remains constant indefinitely, however long the explosion tube may be. For unless such precautions are taken, the results may be misleading.

The photographic method now employed for measuring flame speeds has two great advantages over the older electrical method in that (i) the flame front records its own movement and characteristics which can be analysed at leisure, and (ii) the constancy of the measured speed can be established by two or more photographs of the flame taken over different short lengths of the explosion tube at considerable distances apart. Moreover, in the case of carbonic-oxide-oxygen mixtures, the final establishment of "detonation" (as distinct from the "pre-detonation" phase) can be proved beyond doubt by the pronounced "banded" appearance of the advancing flame. Such appearance, together with subsequent constancy of the flame speed and other features in two successive photographs taken over portions of the explosion tube 60 metres apart, has been our criterion of "detonation" in the present experiments.

Experimental Method.—Our explosion tube and firing arrangements are shown diagrammatically in fig. 3. The source of ignition was a high voltage condenser discharge between electrodes contained in the firing piece A. The flame so initiated then traversed a series of zig-zag passages in the rectangular

* We intend dealing more fully with this aspect of the subject in a subsequent paper.

aluminium "detonating-box," B, similar in design to that originally devised many years ago by Professor G. R. Thompson at the University of Leeds,

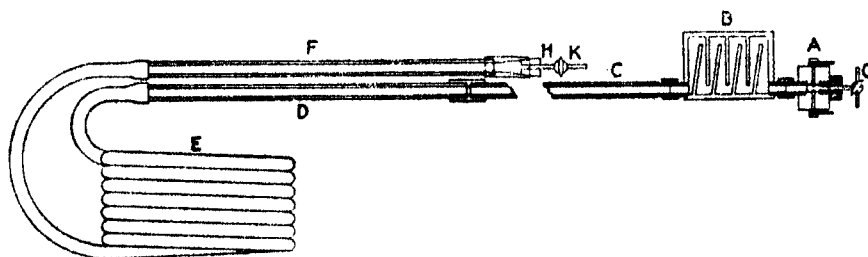


FIG. 3.—Explosion Tube for Detonation Experiments.

which is a most effective means of rapidly setting up "detonation" in a sufficiently explosive gaseous medium. On leaving B, the flame traversed a horizontal section, 3.2 metres long, of glass tubing, C, of selected uniform internal diameter (1.25 to 1.34 cm.) before arriving at the horizontal 1.5 metres section D of the same tubing where its progress was photographed on a vertically moving film by means of a Fraser high speed camera with a 4-inch 2.9 Pentac Dallmeyer lens. The flame then passed onwards through a 60 metres long leaden coil, E, of same internal diameter as the glass section, which terminated in another 1.5 metres long horizontal glass section, F, again of same internal diameter, arranged immediately above and parallel with section D, in such wise that a second photograph of the flame was registered on the same rotating film.

In selecting the glass tubes used in the experiments, special care was taken to ensure both straightness and uniformity of bore in each case. Also, any joints were so made as to preserve exactly the uniformity of bore; this last is an essential condition of accuracy, the attainment of which was attested by the entire absence from the photographs of any effects of "reflection waves" or other disturbing influences.

The end of the explosion tube nearest the firing piece was closed by a three-way wide-bore glass tap, G, while the other end—which during the initial evacuation of the tube and subsequent admission of the experimental mixture thereto had been closed by the large rubber bung, H, carrying a tap, K, which led to a "hyvac" pump and manometer in series—was made "open" by removing the bung immediately before firing the explosive mixture.

It may here be remarked that, whereas ordinarily in exploding moist carbonic oxide-oxygen mixtures, at least a 3 to 5 metres (and in some cases up to a 10

metres) flame run is required for the setting up of detonation, by inserting such a "detonating-box" as B immediately after the firing piece, it was attained quite certainly after a 0.5 metre flame run beyond it, and became quite stabilised during the following 2 metres run.

By the foregoing means two photographs of the horizontally advancing detonation flame were taken, at distances 60 metres apart, on a rotating film 4 inches wide, the (constant and known) vertical speed of which was always adjusted so that the angle subtended with the vertical and the track of the horizontally moving flame front was always between 45° and 50° , such being the condition most conducive to accurate speed-measurements, the probable error being well within 0.5 per cent. The length of each of the two flame movements photographed in each experiment was 1.5 metres, and from fig. 3 it will be seen that the direction of the horizontal flame movement would be reversed during the interval between the taking of the two photographs.

Typical Photograph.—As showing the kind of result obtained, one of the dual photographs so obtained in an experiment with a moist $3\text{CO} + \text{O}_2$ mixture is reproduced in Plate 8. Here the constant vertical film speed was 87.85 metres per second, and the angles subtended with the vertical of the two oppositely moving horizontal flames were both 49.5° , corresponding with flame speeds of 1.775 metres per second in each case. The characteristic "banded" appearance of the two flames, and their otherwise perfect similarity, are remarkable.

Influence of Tube Diameter.—Although, in accordance with the findings both of Berthelot and Vieille and of H. B. Dixon, it has usually been accepted that, provided a certain small limiting diameter is exceeded, the rate of detonation of a given gaseous explosive mixture is independent of the tube diameter, we desired to test the point anew in regard to moist carbonic oxide-oxygen mixtures. Accordingly we made the following two series of experiments.

First Series.—In the first and main series of experiments flame speed measurements were made over the whole detonation-range of moist (*i.e.*, saturated at between 17.5 and 19.0°C . with moisture contents 2.0 to 2.2 per cent.) carbonic-oxide-oxygen mixtures, using tubes of 1.3 cm. internal diameter (all variations being within 0.05 cm. of the mean), the apparatus being arranged as already described, and shown in fig. 3.

Second Series.—A second series of experiments was subsequently made with the same range of explosive mixtures, but using an explosion tube of 2.5 cm. internal diameter. In these experiments, however, the first 5.6 metres section C of the explosion tube was a solid-drawn steel tube of 2.5 cm. internal

diameter, as shown in the diagram, the next 2 metres section D only (where the photograph was taken) being of glass. Moreover, owing to the extreme violence of the explosion, the lead coil E and the glass section F, had to be omitted for "safety" reasons.

The Experimental Results.

The experimental results are set forth below and shown graphically in fig. 4 where velocities in metres per second are plotted as ordinates against CO-contents as abscissæ. From these it will be seen that :—

(1) The "detonation-range" of moist (saturated) carbonic-oxygen mixtures at *circa* 18° and atmospheric pressure lies between about 40 and 80 per cent. CO-contents, as compared with about 15·4 and 94·0 per cent. for their "inflammation range."

In 1·3 cm. Tube.

Percentage CO in mixture ...	50·0	57·6	67·0	71·8	75·6	77·6	80·0
Rate of detonation metres per sec.	1732	1735	1750	1760	1809	1750	1730

In 2·5 cm. Tube.

Percentage CO in mixture ...	57·0	66·6	71·6	75·0	75·4	77·8
Rate of detonation metres per sec.	1752	1795	1825	1870	1840	1780

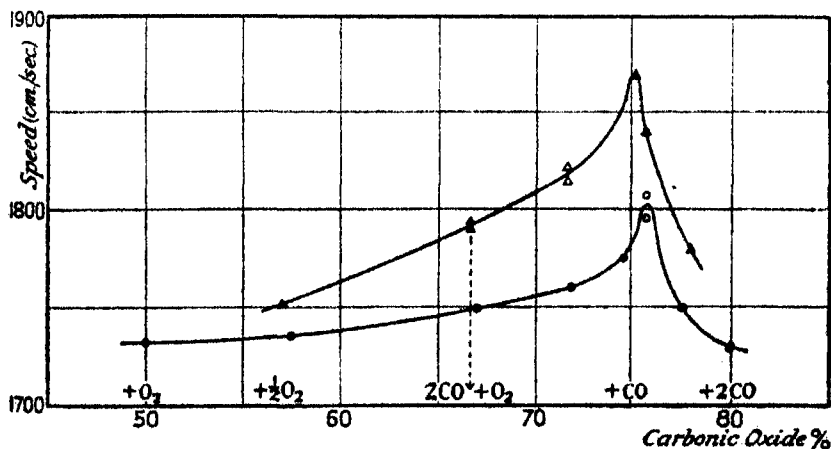


FIG. 4.—Rates of Detonation in Moist CO/O Mixtures.

(2) Within the said range the observed rates of detonation in a tube 1·3 cm. internal diameter all lie between about 1,700 and 1,800 metres per second.

(3) Undoubtedly the rate of detonation of a given CO-O_2 mixture is not quite independent of variations in tube diameter within the limits examined by us, the rate being sensibly higher in a tube of 2.5 than in a tube of 1.3 cm. internal diameter. In this connection it may be added that we have found a glass tube of 0.36 cm. internal diameter to be the narrowest in which a true detonation could be set up and maintained by our method in a moist $2\text{CO} + \text{O}_2$ mixture at 17.5° and 765 mm. pressure, the speed of such detonation being 1,575 as compared with 1,750 in a tube of 1.3 cm. internal diameter and with 1,790 metres per second in a tube of 2.5 cm. internal diameter.

(4) In both series of experiments there was a well-marked maximum rate of detonation at the $75\text{CO}/25\text{O}_2$ mixture composition. This observation harmonised well with what had already been found (p. 543) regarding the maximum "rate of inflammation" in carbonic oxide-oxygen mixtures; which occurred at very nearly the same point on the speed-composition curve (*vide* fig. 1).

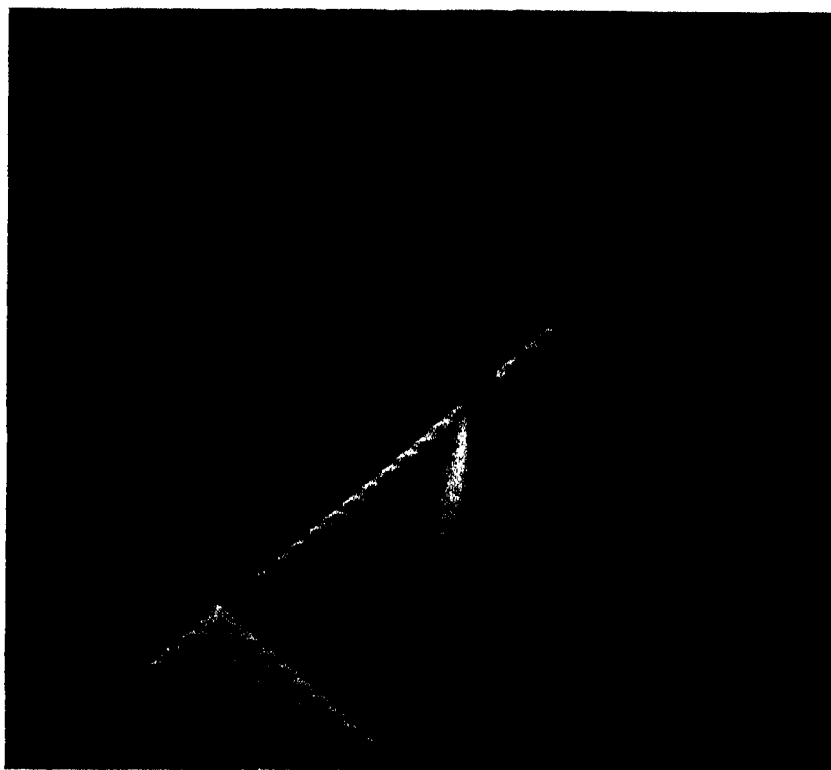
(5) Attention is particularly directed to the fact that, whereas an excess of CO up to $3\text{CO} + \text{O}_2$ over the theoretical $2\text{CO} + \text{O}_2$ proportion increased the flame speed in both "inflammation" and "detonation," similar excess of oxygen always diminished it. Thus, for example, in the first series of "detonation" experiments we find:—

Mixture.....	$2\text{CO} + \text{O}_2$	$2\text{CO} + \text{O}_2 + \text{CO}$	$2\text{CO} + \text{O}_2 + \text{O}_2$
Speed (metres per second)	1750	1775	1732

Discussion.

Undoubtedly the most interesting features of our results for the moist carbonic oxide-oxygen mixtures are those referred to under (4) and (5), namely, the occurrence of so well-defined a maximum flame speed at *circa* the $3\text{CO} + \text{O}_2$ instead of at the $2\text{CO} + \text{O}_2$ mixture in both "inflammation" and "detonation," showing that whereas an excess of carbonic oxide (up to such limit) increased, a corresponding excess of oxygen always diminished, the flame speed. And from the curves shown in fig. 2 it is evident that this circumstance is not materially altered by diluting the medium with either argon, helium or nitrogen. It should also be noted that G. I. Finch and W. L. Patrick have recently observed a pronounced maximum rate of cathodic combustion for moist carbonic oxide-oxygen mixtures at a non-sputtering cathode at approximately the $4\text{CO} + \text{O}_2$ composition.*

* 'Proc. Roy. Soc.,' A, vol. 129, p. 656 (1930).



Detonation in a $3\text{CO} + \text{O}_2$ Mixture.

Such results can hardly mean other than that in the case of moist carbonic oxide-oxygen mixtures the point of maximum flame-speed is principally determined not by the density of the medium, nor by flame temperature, nor yet by suppression of CO_2 -dissociation nor the like, but rather by the CO -concentration itself. And such a conclusion points to the combustion of moist carbonic oxide being conditioned by a prior "excitation" of its molecules, which are then, but not otherwise, rendered combustible.

In conclusion we desire again to acknowledge our indebtedness to Messrs. Nobels Explosives, Ltd. (I.C.I.) for their continued generous support of this and cognate researches, including the personal grant which enables one of us (R.P.F.) to devote his whole time to them.

The Symmetric Spherical Oscillator, and the Rotational Motion of Homopolar Molecules in Crystals.

By T. E. STERN, B.Sc., Princeton University ; Trinity College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received December 6, 1930.)

§ 1. *Introduction, and the Symmetric Spherical Oscillator.*

In a recent paper, L. Pauling* has discussed the motion of molecules in crystals. By the use of approximate methods, criteria are deduced in that paper for determining when the motion of molecules in crystals is "rotational," and when it is "oscillational" about positions of equilibrium. While it served Pauling's purpose, the investigation did not go deep enough to satisfy the needs of the present author, who desired information about the statistical weights of the lowest quantum states of molecules in crystals, more certain and definite than that provided by Pauling's analysis. The present more rigorous investigation was accordingly undertaken. The results go somewhat beyond the author's needs, but they are perhaps interesting in themselves. The investigation involves a problem in quantum mechanics which is capable of exact treatment, without the use of perturbation methods.

We imagine a homopolar molecule of type X_2 free to rotate in a field of force of axial symmetry. Symmetry considerations show that if a certain orientation

* L. Pauling, 'Phys. Rev.', vol. 36, p. 430 (1930).

is one of equilibrium, then the orientation obtained by reversing the molecule end for end will also be one of equilibrium; and we see also, if the orientation of the molecule is specified by the co-ordinates θ, ϕ (the axis of θ being the axis of equilibrium), that the potential function $V(\theta)$ of the homopolar molecule must be symmetric about the equatorial circle $\theta = \pi/2$. We suppose that our molecule is free from axial spin. If $V(\theta)$ can be expanded in a Fourier series, then it can be expanded in a Fourier series made up of cosines of even multiples of θ . A good first approximation will be obtained by taking only the first two terms of this series; higher terms can be taken account of later, if desired, by a perturbation method. We therefore consider, with Pauling, the potential function

$$(1) \quad V = V_0 (1 - \cos 2\theta).$$

We desire solutions of the wave equation

$$(2) \quad \nabla^2 \psi + 8\pi^2 I (W - V) \psi / h^2 = 0$$

in the form

$$(3) \quad \psi = F(\theta) e^{m\phi},$$

subject to the conditions that ψ must be single-valued, and that $|\psi|$ must be bounded, over the surface of the θ, ϕ sphere. W is the total energy of the molecule as far as rotations about its centre of mass are concerned, I is its moment of inertia, and h is Planck's constant.

We see at once that m must be an integer which can be positive, zero, or negative in value. Make the substitutions (1), (3), and

$$(4) \quad \begin{cases} x = \cos \theta \\ \mu = (W - 2V_0) 8\pi^2 I / h^2 \\ \lambda^2 = 16\pi^2 I V_0 / h^2 \end{cases}$$

in equation (2). We obtain

$$(5) \quad (1 - x^2) F'' - 2xF' + (\mu + \lambda^2 x^2 - m^2 / (1 - x^2)) F = 0.$$

Solutions are desired which are finite within the interval $-1 \leq x \leq 1$. This equation has been considered by A. H. Wilson* among others; corresponding to any value of λ there exist certain eigen-values of μ for which our conditions will be fulfilled. Make the substitution

$$F = (1 - x^2)^{M/2} y,$$

* A. H. Wilson, 'Proc. Roy. Soc.,' A, vol. 118, p. 628 (1928).

where $M = |m|$. Then our desired solutions are of two different types. We can represent y by a series of even powers of x , or by a series of odd powers of x . The two types refer in general to different values of μ .

Wilson gives the equation

$$(6) \quad M(M+1) - \mu \\ = \frac{1 \cdot 2 \lambda^2}{(M+2)(M+3) - \mu} - \frac{3 \cdot 4 \lambda^2}{(M+4)(M+5) - \mu} + \frac{5 \cdot 6 \lambda^2}{(M+6)(M+7) - \mu} - \dots$$

for the eigen values of μ corresponding to solutions of the even type, and the equation

$$(7) \quad (M+1)(M+2) - \mu \\ = \frac{2 \cdot 3 \lambda^2}{(M+3)(M+4) - \mu} - \frac{4 \cdot 5 \lambda^2}{(M+5)(M+6) - \mu} + \dots$$

for the eigen-values of μ corresponding to solutions of the odd type. These continued fractions are convergent for all values of λ and μ ; and from them it is possible to calculate numerical values of μ corresponding to arbitrarily chosen values of λ .

The author has used these equations to calculate values of μ for the first seven eigen-states of the spherical oscillator, for integral values of λ up to and including six. The method used was to locate the roots by changes in sign, in the difference between the members of the equation used, when the root was passed; and to estimate by interpolation the position of the root within the "bracketing" values. The bracket used was unity, and values given by the graph 1 may be relied upon to well within a unit. It is not practical to calculate very large values of the roots accurately by this method, because of the great labour involved in using a sufficiently large number of terms in the continued fraction each time one tries to locate one end of a bracket. Methods will be described presently for obtaining approximations to the eigen-values of μ corresponding to large values of λ .

In fig. 1 are shown the eigen-values of μ corresponding to values of λ up to six, for some of the lowest energy levels. The dotted curve $(3, \pm 2)$ is not accurate, and was drawn merely to complete the second vibrational level. If λ is zero, it is obvious that our wave equation (2) is merely that of the spatial rotator; and we find as we expect the corresponding values of μ . Accordingly, the curves may be numbered by the use of n and m , the quantum numbers of the

spatial rotator from which they originate at the left-hand side of the diagram for small λ . The symmetry properties of the eigen-states will, of course, not

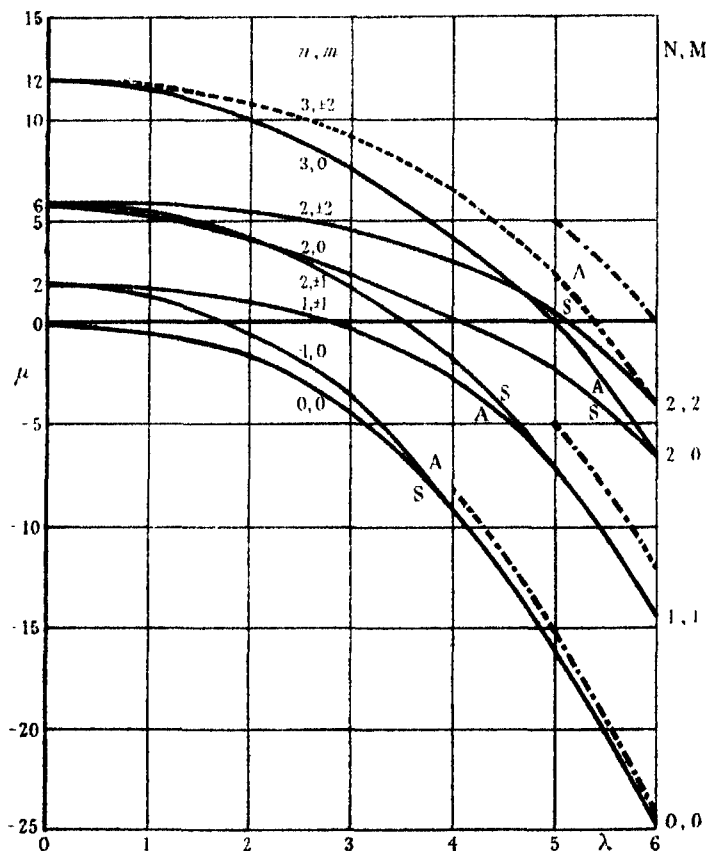


FIG. 1.

alter when λ is increased, so that we may denote by A and by S respectively the states which are antisymmetrical, and symmetrical, in the reversal of the radius vector θ , ϕ end for end. The component of angular momentum about the axis $\theta = 0$ will not change as λ is increased, so that m will remain a good quantum number. On the other hand, n loses its significance for large values of λ . We shall find that there will always be a degeneracy associated with non-zero values of M , corresponding to both positive and negative values of m ; and for this reason we use M rather than m as the quantum number for values of λ greater than zero.

As pointed out above, this analysis does not tell us much about the behaviour

of the solutions for large values of λ . However, Wilson* gives the following asymptotic expansion for μ :

$$(8) \quad \mu = -\lambda^2 + 2\lambda(r + M + 1) + O(1/\lambda)$$

corresponding to the fundamental set of solutions:

$$(9) \quad \begin{cases} y_1 = e^{\lambda \cos \theta} \{(\sin \frac{1}{2}\theta)^r / (\cos \frac{1}{2}\theta)^{2(M+1)+r} + O(1/\lambda)\} \\ y_2 = e^{-\lambda \cos \theta} \{(\cos \frac{1}{2}\theta)^r / (\sin \frac{1}{2}\theta)^{2(M+1)+r} + O(1/\lambda)\}. \end{cases}$$

The solutions (9) fail at $\theta = \pi$ and at $\theta = 0$, and it is possible besides that there should be a constant term in (8). But if the first two terms of (8) are correct, then from the definition of asymptotic series we know that the error, resulting from using only the first two terms in (8) is $\varepsilon\lambda$, where $\varepsilon \rightarrow 0$ as $\lambda \rightarrow \infty$. In Wilson's paper, it is stated that r must be an integer, but we shall show that we can take only positive even values or zero for it.

From (4), (8), and the definition of asymptotic series, we have for large λ

$$W = h\nu_0(1 + r + M) \left(1 + \frac{\varepsilon}{2(r + M + 1)}\right)$$

where

$$\nu_0 = \frac{1}{\pi} \left(\frac{V_0}{I}\right)^{1/2},$$

the frequency of vibration which the system would have, for small amplitudes of vibration, if it were classical. That is, nearly, for large values of λ and with a percentage error which approaches 0 as $\lambda \rightarrow \infty$,

$$(10) \quad W = h\nu_0(N + 1),$$

where

$$N = r + M.$$

This is the same as the equation giving the energy levels of the plane oscillator, which ought to be a good approximation to our system if λ is very large and if the energy level of our system is a low one. The broken curves in fig. 1 represent equation (8) for values of N equal to 0, 1, and 2.

It is now necessary to investigate the degeneracy of the various energy states of our wave equation for large λ . To begin with, corresponding to any value of N in equation (10) greater than 0, there are various ways of choosing r and M . We shall show that r must be even. Further, corresponding to each choice of r and M , there will be two choices of m if $M > 0$, and corresponding to each of these there will be two wave functions, one symmetric, the other anti-

* Wilson, *loc. cit.*

symmetric in reversals of the radius vector end for end, made up of linear combinations of the two solutions given by (9).

We show that r must be even as follows. When λ is very large, we imagine equation (2) solved by a perturbation method. The unperturbed wave equation is taken as that of the plane oscillator, and its solutions involve the well-known Hermite polynomials. The energy levels of the plane oscillator are given accurately by (10), and for any value N_1 of N there are $N_1 + 1$ linearly independent wave-functions. In particular, we can choose as our $N_1 + 1$ wave-functions the eigen-functions corresponding to the $N_1 + 1$ eigen-values of the angular momentum* $-N_1, -N_1 + 2, -N_1 + 4, \dots, N_1 - 2, N_1$; measured in units $\hbar/2\pi$. When we apply the necessary perturbation to the plane oscillator equal to the difference between the Hamiltonians of the spherical and plane oscillators, we may succeed, possibly, in splitting up our former energy levels to some extent; but we will not obtain any new eigen-values of the angular momentum—which now is the component of angular momentum of the spherical oscillator about the axis $\theta = 0$. M must still differ from N_1 by zero or an even integer.

Corresponding, therefore, to any value N_1 or N there are $2(N_1 + 1)$ linearly independent wave-functions; of these $N_1 + 1$ are symmetrical, and $N_1 + 1$ are anti-symmetrical, in reversals of the radius vector end for end.

The relation between the cases of small and large λ is shown graphically in fig. 2. The number of linearly independent wave-functions is denoted by K .

§ 2. *The Rotational Motion of Homopolar Molecules in Crystals.*

From here on our investigation is similar to Pauling's. He points out that the molecules can be said to "rotate" if the difference between the energies of the wave-functions for a given N value is large compared with the difference between the energies of consecutive N levels, since the probability of reversals of the molecule end for end is then large; and that the molecule can be said to

* We can show that these are the eigen-values of the angular momentum as follows. We write the wave-equation of the plane oscillator in plane polar co-ordinates: r, θ . If the substitution is then made $\psi = f(r) \exp(i\ell\theta)$ (see a paper "The Diamagnetism of the Free Electron," C. G. Darwin, 'Proc. Camb. Phil. Soc.,' as yet unpublished (December, 1930). We must let $\omega \rightarrow 0$. We find for eigen-values of the angular momentum $\ell\hbar/2\pi$, where ℓ has any integral value, positive, negative, or zero; and we find for the corresponding eigen-values of the energy $W = \hbar\nu_0(2a + |\ell| + 1)$, where a is a positive integer or zero. We must take $N = 2a + |\ell|$, and we then see at once that for a given value N_1 of N the possible eigen-values of the angular momentum of the plane oscillator are those given in the text above.

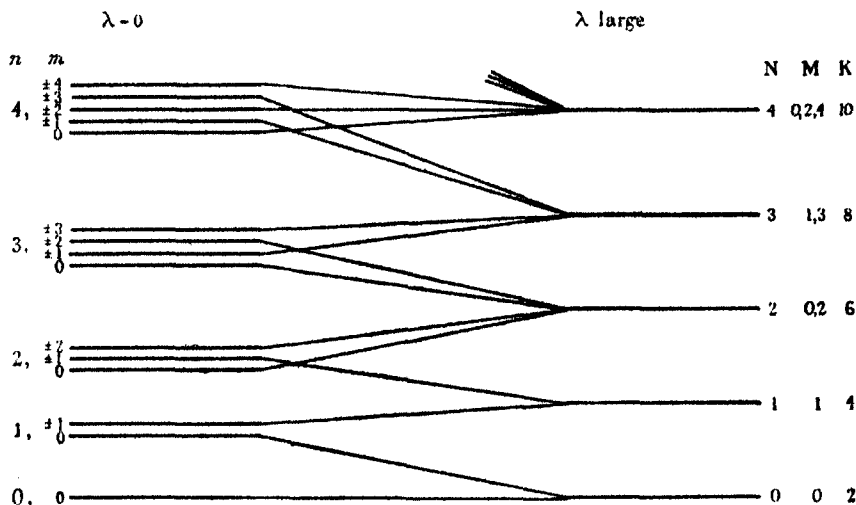


FIG. 2.

"oscillate" about positions of equilibrium if the difference between the energies of the wave-functions for a given N is small compared with the difference between the energies of consecutive N levels. The transition between the two cases seems from an inspection of fig. 1 to occur roughly along the axis $\mu = 0$; which corresponds to $W = 2V_0$. We might have anticipated this from the form of the potential function. We can obtain exactly the same criteria as Pauling's for distinguishing between the two cases, without any difficulty; but it seems to us to be simpler to proceed as follows. For "rotation" to occur, we are to have $W > 2V_0$; and regardless of the nature of the energy levels of the molecules, the molecules will not be likely, statistically, to possess this energy until the temperature T of the crystal rises to be comparable with $2V_0/k$, where k is Boltzmann's constant. Therefore, roughly, "rotation" occurs if

$$T > 2V_0/k$$

and "oscillation" occurs if

$$T < 2V_0/k.$$

These criteria are exactly equivalent to Pauling's, but can be derived more simply and are in a simpler form. Actually, the probability that a molecule will "rotate" is given roughly by

$$P = \exp. (-2V_0/kT).$$

For the calculation of V_0 , we refer the reader to Pauling's paper.

The writer wishes to express his thanks to Mr. R. H. Fowler for his many helpful criticisms and his advice.

Fine Structure in the Mercury Singlet Terms.

By S. TOLANSKY, B.Sc., Armstrong College, Newcastle.

(Communicated by T. H. Havelock, F.R.S.—Received December 9, 1930.)

1. *Introduction.*

The fine structure occurring in a number of line spectra has been reasonably accounted for by the theory of nuclear spin, but up to the present the complexity of the fine structure in mercury lines has remained unexplained, more lines occurring than theory demands. Because of the weakness of the singlets in the sources usually employed most of the investigations on mercury fine structure have been carried out on triplet and intercombination lines. The fine structures in the singlet series should yield more readily to analysis than in the triplet series, being simpler, and for this reason are investigated here. A comprehensive survey of the experimental work done up to 1926 in mercury was given by Ruark* who succeeded in accounting for the majority of the components in several triplet lines by giving a number of levels a threefold multiplicity. Only one singlet level 6^1P_1 was discussed and the multiplicity attributed to this was seven.

In a previous communication† an account was given of a method for increasing the relative and intrinsic intensity of the singlet series and of inter-combination lines involving upper singlet levels. The series $6^1P_1 - m^1S_0$, $7^1S_0 - m^1P_1$ and $7^3S_1 - m^1P_1$ are particularly strengthened and these have been examined for fine structure with a Fabry-Perot interferometer. It was stated in a preliminary note‡ that $\lambda 4916$ ($6^1P_1 - 8^1S_0$) had four components and that the members of the series $7^1S_0 - m^1P_1$, $7^3S_1 - m^1P_1$ were sextet. These observations are now somewhat extended, fainter components having been found. Whilst this paper was in the course of preparation, a communication was received from Venkatesachar and Sibaiya§ giving the structures of some of these lines. Venkatesachar also stated, that in a short note to 'Nature,' which was overlooked by the writer, Hansen|| found that $\lambda 4916$ was a quintet. These results will be discussed later.

* 'Phil. Mag.' vol. 1, p. 177 (1926).

† 'Proc. Phys. Soc. Lond.,' vol. 42, p. 556 (1930).

‡ 'Nature,' vol. 126, p. 433 (1930).

§ 'J. Mysore Univ.,' vol. 5, p. 145 (1930).

|| 'Nature,' vol. 119, p. 237 (1927).

2. *Experimental Procedure.*

Many false structures have been recorded in mercury and much confusion has resulted from the common occurrence of self reversal in the sources employed, usually cooled low current arcs. In this investigation a low pressure high frequency electrodeless discharge in pure mercury vapour was used, since it is in this discharge that the enhancement of the singlets takes place. The experimental arrangements for producing the discharge were identical with those previously described* but the tube was modified. A Mullard D.O. 40 valve was caused to oscillate on a wave-length of about 7 metres, and this was coupled inductively to a pair of wires of variable length connected to strips of metal foil wrapped round the ends of the tube. When the coupled circuit was in tune the tube glowed brightly, the singlets being stronger than in a low current arc. The strengthening of the singlet lines increased with lower current density and with lower temperature. In order to obtain the maximum amount of light, a pyrex tube 5 feet long of 1 inch internal diameter was employed. The tube was highly evacuated by means of a mercury vapour pump and charcoal in liquid air, being thoroughly baked whilst pumping. About half a cubic centimetre of pure mercury was distilled into a side limb. The ends were blown into round windows and the observations carried out end on through the 5 feet depth of vapour. As shown in the previous paper there is no self absorption of the singlet series in the high frequency discharge, whilst the triplets are very strongly absorbed, particularly the lines λ 5461 and λ 4046. These lines involve metastable levels, and as the pressure in the tube is very low these levels are favoured, thus increasing the absorption. This produces an interesting effect. When viewed at right angles to the tube, the discharge is a greenish blue: when viewed end on, it is red, due to the absorption of the green line and the strengthening of the red singlets because of the greater depth of view.

The high frequency discharge is eminently suited to fine structure work since there are no strong electric fields and the pressure at which bright discharges can be obtained is usually very low. The tube runs quite cold and as the vapour pressure of the mercury is only of the order of 0.001 mm., the result is the production of lines much finer than can be obtained in any type of cooled arc. A source of difficulty lies in the fact that the high frequency discharge drives vapours into the walls of the tube with very great violence, particularly at the ends. The result is that after some hours the windows

* 'Proc. Phys. Soc. Lond.,' *loc. cit.*

become coated with a film of mercury which reduces the intensity of the source very considerably. This film is not removed by heating to a dull red heat *in vacuo*. It was observed that the parts of the tube under the electrode remained free from film.

The ends of the tube were covered with thin copper foil electrodes, 10 cm. long, each having slots 1 cm. long and 2 mm. wide cut in them. With this device the windows were kept almost free from film, one tube remaining clear for some 150 hours before accidental destruction. A slight film was deposited after long running, but the shielding of the electrode was sufficiently effective in keeping this so thin as hardly to affect the transparency of the window. The shielding was more effective when the tube had rounded ends.

The lines were examined for fine structure with a Fabry-Perot (N.71) interferometer crossed with a large quartz (E.1) spectrograph, both by Hilger. The interferometer has quartz plates with a 6 cm. aperture and a variable separation. Ilford soft gradation panchromatic plates were used for the red lines and Ilford Golden Isozenith plates were also used for the blue. In all over 60 photographs were taken with plate separations varying from 3 to 100 mm., and exposures varying from 5 minutes to 7 hours. This was found to be necessary in order to remove any ambiguity as to overlapping orders, etc., and because of the very marked intensity differences in some of the structures.

The length of the exposures was limited by barometric fluctuations.* For the centre of the ring system of given wave-length λ we have $n\lambda = 2\mu t$, where n is the order of interference at the centre, t the plate separation and μ the refractive index of the air. Both pressure and temperature variations affect μ , but since the temperature can be reasonably controlled the main disturbance is pressure change, which broadens the fringes. We thus get

$$\lambda \, dn = 2t \, d\mu \cdot$$

therefore

$$dn = \frac{2t}{\lambda} d\mu,$$

since $\frac{\mu - 1}{\rho}$ is constant, ρ being the density of the gas

then

$$d\mu = \frac{d\rho}{\rho} (\mu - 1)$$

therefore

$$dn = \frac{2t}{\lambda} \frac{d\rho}{\rho} (\mu - 1).$$

* W. E. Williams, "Applications of Interferometry," p. 86 (Methuen, 1930).

This gives dn , the fractional broadening of a fringe due to a given change in air density. With the sodium D lines and a change of pressure of 1 mm. dn is 0.013 for a 1 cm. gap. Since the actual fractional difference of some of the components is about 0.1, it is seen that a millimetre pressure change can seriously affect the definition. In rare cases only, could a 3-hour exposure be exceeded.

3. *Mode of Reduction.*

In the Fabry-Perot interferometer we have for any pair of components of a line $d\nu = dn/2\mu t$ where $d\nu$ is the frequency difference between the components and dn the difference of the orders of interference at the centre of the two ring systems. dn is usually less than unity in practice. It is sufficiently accurate for the present purpose to take $d\nu = dn/2t$. t is given by a scale on the instrument, reading to 0.005 mm., which greatly exceeds the accuracy to which dn can be determined. It can be easily shown that $d_p^2/d_{p+1}^2 = (\epsilon + p - 1)/(\epsilon + p)$, where d_p , d_{p+1} are the diameters respectively of the p th and $p + 1$ th rings of any given component and ϵ the fractional order at the centre. This gives $\epsilon = d_{p+1}^2/(d_{p+1}^2 - d_p^2) - p$. Further, it can be shown that $d_{p+1}^2 - d_p^2 = 8k^2f^2/n_0$ where k is the magnification factor of the spectograph, f the focal length of the image forming lens of the interferometer and n_0 the absolute value of the order of interference at the centre. This is very high and may be taken as the same for all the components of a line, so that $d_{p+1}^2 - d_p^2$ should be a constant for all the components. Usually three or four rings were measured with the smaller gaps, and more with the larger. The squares of the diameters were arranged in a table and the differences of adjacent values taken, giving several values, often about 16. The squares divided by the weighted mean of these differences gave the fractional order at the centre plus an integer. The deviations of the differences from the mean difference enable weights to be given to the individual diameters so that the final accuracy of the results is very much increased. For any pair of components with fractional values ϵ_1 and ϵ_2 , $dn = \epsilon_1 - \epsilon_2$, so that

$$d\nu = (\epsilon_1 - \epsilon_2)/2t.$$

4. *Experimental Observations.*

A. *The Series $6^1P_1 - m^1S_0$.*—Of this series only one line $\lambda 4916$ ($6^1P_1 - 8^1S_0$) gave reliable data since the next members were in a region where the resolving power of the interferometer was relatively poor.

λ 4916.

This line has long been considered as single and is given as such by Ruark. As already mentioned, Hansen finds five components whilst Venkatesachar and Sibaiya ascribe a coarse octet structure to it. This line was examined with plate separations varying from 3 mm. to 100 mm. Most of the plates agree extremely well. The separations, given in thousandths of a wave-number, are probably accurate to one unit. Table I and fig. 1 show a comparison of the structure observed with those recorded by Hansen and by Venkatesachar and Sibaiya. Intensities are only visual estimates in all cases. In the present work the relative intensities of widely different lines were estimated by using lines of intermediate intensity in a step up ratio.

Table I.

Hansen.	Tolansky.	Venkatesachar and Sibaiya.
—	—	+571 (2)
—	—	+306 (5)
+ 98 (2)	+ 98 (1) <i>a</i>	+240 (1)
+ 56 (4)	+ 55 (4) <i>b</i>	+ 83 (2)
0 (10)	0 (30) <i>c</i>	0 (10)
— 66 (3)	— 62 (3) <i>d</i>	—124 (3)
—121 (5)	—128 (2) <i>e</i>	—364 (2)
		—612 (1)

The structure given by Venkatesachar and Sibaiya differs markedly from the other two, which agree very well. A search was made for this coarse structure. The interferometer was set with a 4 mm. gap, at which separation the extreme components given by them should be approximately midway between adjacent orders. The main component was heavily exposed in 5 minutes, yet no sign of this coarse structure appeared after 7 hours. A Cooper Hewitt low current arc also showed no indication of this structure.

The structures may actually differ in the different discharges but this is not likely since the Cooper Hewitt arc did not show any variation. If the coarse structure is spurious, strong self reversal, or ghosts in the interferometer used are possible causes.*

The most noticeable fact concerning the structure of λ 4916 is the great relative intensity of the main component, which is considerably greater than

* Dr. Hansen informs me that he also finds no trace of the coarse structure using Lummer plates and a Fabry-Perot interferometer. He states that the separations given by him were calculated from one plate only and are not therefore to be considered as very reliable. The agreement with the present observations is nevertheless extremely good.

the sum of the intensities of all the others. This is not likely to be due to the fact that the line is a group of unresolved components. If it is, the components

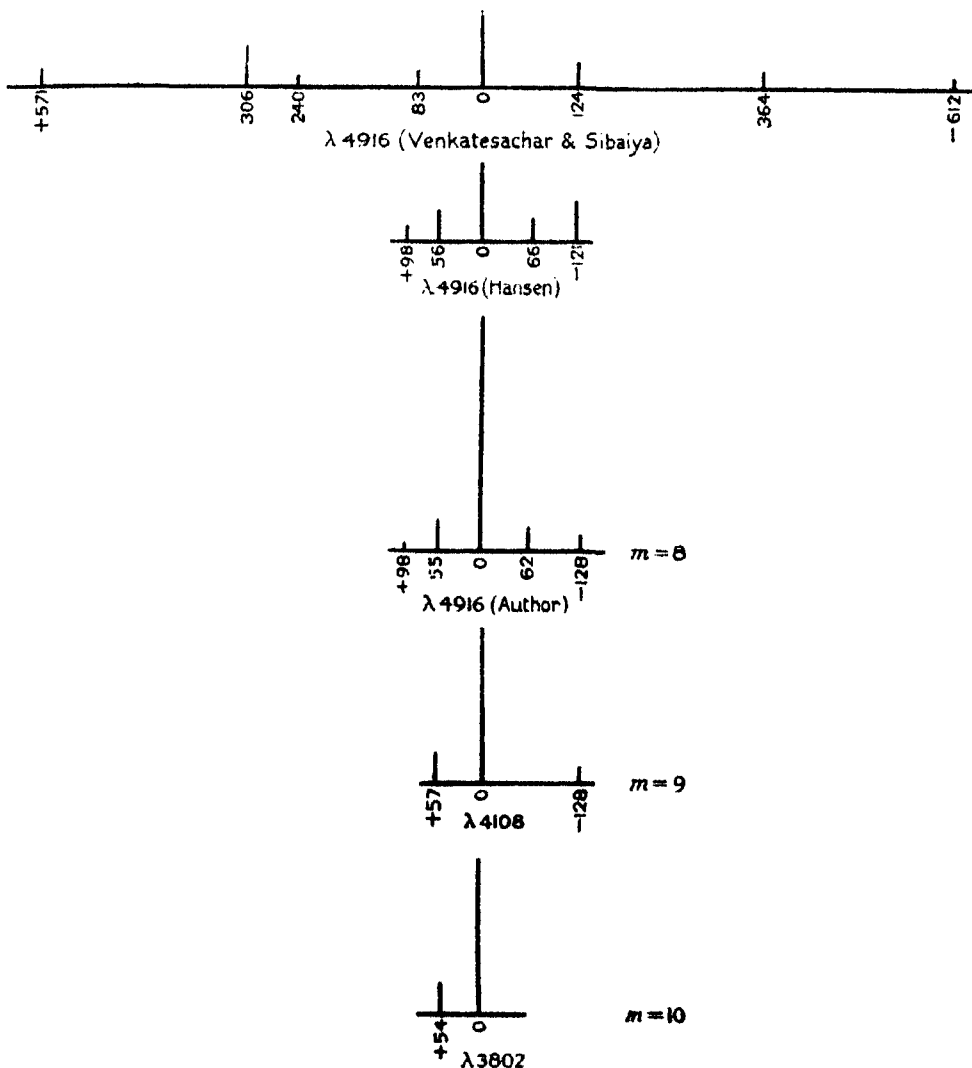


FIG. 1.—Structure of Lines of $6^1P_1 - m^1S_0$ Series. Intervals in $\text{cm.}^{-1} \times 10^{-3}$.

are extremely close together since the line is not split up with plate separations of 10 cm. and is so narrow that components must certainly be less than $0.002 \text{ \AA.}$ apart. There is a marked difference between the intensities recorded and those given by Hansen. It was previously shown* that the satellites of $\lambda 5461$ are

* 'Proc. Phys. Soc. Lond.,' *loc. cit.*

more nearly equal in intensity in the high frequency discharge than in the arc, and this is due probably to the relatively greater absorption in the high frequency discharge. If the source used by Hansen (a water cooled Lummer lamp) absorbs λ 4916 more than in that used here,* then a similar effect will be expected. Fig. 1 shows that Hansen's intensities are more nearly equal than those recorded here. Any type of arc is likely to absorb λ 4916 to a greater extent than the extremely low pressure high frequency discharge. Selective self absorption may then account for the difference.

It was due to the great differences in intensities that the line was first recorded as single.

*Structures of λ 4108 ($6^1P_1 - 9^1S_0$) and λ 3802 ($6^1P_1 - 10^1S_0$).—*An attempt was made to obtain the structures of these two lines since they are the next two members of the series to which λ 4916 belongs. They fall in a region unsuited to the Fabry-Perot used, so that the fringes were poor and only the stronger components could be observed. It is intended to investigate these lines later with a more suitable interferometer since their complete structures would enable the structure of the 6^1P_1 level to be determined. λ 4108 showed three components and λ 3802 two.

λ 4108.	λ 3802.
$+ 57 \pm 1$ (2)	
	$+ 54 \pm 5$ (2)
0 (10)	
	0 (10)
$- 128 \pm 2$ (1)	

The accuracy of measurement is poor in the case of λ 3802. The structures are shown graphically in fig. 1.

B. *The Series $7^1S_0 - m^1P_1$.—*Two members of this series, namely, λ 6716 ($7^1S_0 - 8^1P_1$) and λ 6234 ($7^1S_0 - 9^1P_1$) were examined. The first gave a sextet structure, the second showed a seventh faint component. There is a rapid falling off in plate sensitivity towards λ 6716 and this line photographed much weaker than the next member of the series. One would have expected it to have shown the same number of components as λ 6234, but the seventh, if there, would be too faint to be photographed. Venkatesachar and Sibaiya attribute a quintet structure to the line λ 6716.

Structure of λ 6716.—Most of the measurements were carried out with plate

* See also Metcalfe and Venkatesachar, 'Proc. Roy. Soc.,' A, vol. 105, p. 520 (1924).

separations of 7 mm. to 9 mm., but for the closer components a 25 mm. gap was used. Three hour exposures were usually employed. The observed structure, together with that given by Venkatesachar and Sibaiya is shown on Table II.

Table II.

Venkatesachar and Sibaiya.	Tolansky.
+120 (2)	+220 ± 4 (1) <i>a</i>
0 (8)	+122 ± 3 (3) <i>b</i>
-120 (10)	0 (30) <i>c</i>
-260 (5)	-122 ± 1 (20) <i>d</i>
	-230 ± 4 (5) <i>e</i>
	-279 ± 1 (5) <i>f</i>

The extreme limits for the separation errors are indicated in the second column. The probable error is less than the range indicated.

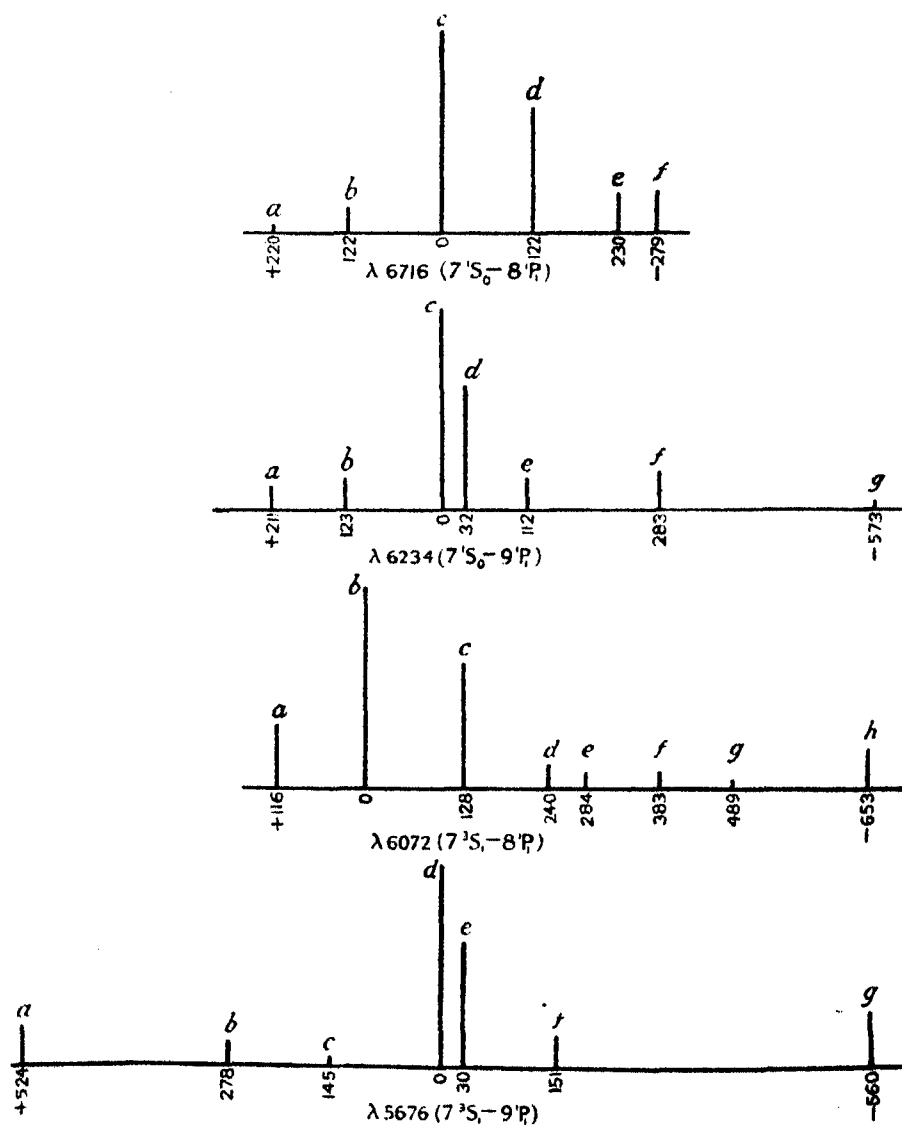
There is good agreement for the stronger pair *cd* only. Venkatesachar and Sibaiya give a component -260 which is obviously the pair *ef* but unresolved, since the 25 mm. gap was needed to separate these completely. Their intensities differ from those given here, the cause of which may also be absorption. A weaker source and an inferior resolving power will explain the differences. The observed structure is shown graphically in fig. 2.

Structure of λ 6234.—This shows seven components. With plate separations of 6 mm. to 9 mm. the appearance is that of a very strong main line with five weaker satellites fairly symmetrically distributed. The main component was resolved as a close doublet with a 25 mm. gap so that one of the weaker lines was taken as the standard from which differences were calculated. Only the two longest exposures, 4 hours and 7 hours showed the seventh component. The structure is given in Table III and fig. 2.

Table III.

+88 ± 4 (3) <i>a</i>
0 (4) <i>b</i>
-123 ± 1 (30) <i>c</i>
-155 ± 1 (20) <i>d</i>
-235 ± 1 (4) <i>e</i>
-406 ± 1 (5) <i>f</i>
-696 ? (1) <i>g</i>

C. *The Series $7^3S_1 - m^1P_1$.*—Two members, λ 6072 ($7^3S_1 - 8^1P_1$) and λ 5676 ($7^3S_1 - 9^1P_1$), were examined. The first was found to have eight

FIG. 2.—Structures of $S - ^1P_1$ Lines.

components, and the second, which was much weaker, showed seven. Venkatesachar and Sibaiya have examined $\lambda 6072$ in the arc and find five components.

Structure of $\lambda 6072$.—Plate separations varying from $4\frac{1}{2}$ mm. to $8\frac{1}{2}$ mm., with exposures of 3 hours were employed. A certain amount of trouble was caused by one component, which was reasonably strong and so far from the main

pair, that it overlapped into the next order blurring different components for different gaps. The observed structure is compared with that given by Venkatesachar and Sibaiya in Table IV.

Table IV.

Venkatesachar and Sibaiya.	Tolansky.
+122 (7)	+116 ± 2 (7) <i>a</i>
0 (10)	0 (30) <i>b</i>
-119 (5)	-128 ± 2 (20) <i>c</i>
-244 (1)	-240 ± 2 (3) <i>d</i>
-320 (3)	-284 ± 3 (2) <i>e</i>
	-383 ± 4 (2) <i>f</i>
	-489 ± 3 (1) <i>g</i>
	-653 ± 1 (5) <i>h</i>

The agreement is poor. The source used by Venkatesachar and Sibaiya is probably weaker, accounting for the absence of the fainter lines, since only the strongest are recorded by them. The intensities are considerably different, as in the case of the previous lines. The structure is shown graphically in fig. 2.

Structure of λ 5676.—For gaps of 5 mm. to 12 mm., and with the longest exposures, the line showed a strong main component with five weaker satellites, the main component being resolved as a close doublet at 25 mm. See Table V and fig. 2.

Table V.

+524 ± 2 (5) <i>a</i>
+278 ± 4 (3) <i>b</i>
+145 ± 3 (1) <i>c</i>
0 (30) <i>d</i>
- 30 ± 1 (20) <i>e</i>
-151 ± 2 (4) <i>f</i>
-560 ± 2 (7) <i>g</i>

There are several factors to be considered in discussing the observed structures in relation to those given by Venkatesachar and Sibaiya. There has often been a good deal of disagreement in recorded structures due to the following causes. Imperfections in the interferometers used have resulted in ghost images, varying degrees of self-reversal have produced either spurious lines or apparent displacements, insufficient resolving power has caused a group of lines to be classified as one, with weaker sources fainter components have been missed, and finally it is possible that structures actually differ in

different types of discharge. As regards the relative merits of different types of interferometer, the Fabry-Perot, particularly if the gap is continuously variable, has important advantages in the less refrangible part of the spectrum. There is no liability to false images, and ambiguities arising from the overlapping or superposition of orders can be completely resolved by choosing suitable gaps.

It is evident that the source used by Venkatesachar and Sibaiya was much weaker than that employed here. The resolving power of their Lummer plates does not appear to have been adequate, since a pair of close components in λ 6716 is recorded by them as one. It is very improbable that the structures recorded here have been affected by reversal since they remained the same under very varying conditions of discharge. For instance the same structure was obtained when viewing end on through columns of vapour varying in length from 10 to 150 cm. and also in the discharge through a capillary tube 1 cm. long and 2.5 mm. bore. The singlets were much weaker in the latter case on account of the higher temperature and pressure, so that only the stronger components were observable. With this discharge the separation of the main pair of components of λ 6716 was 122 and 121 on two different plates, that is, identical with the value, 122, for the long tubes. If this structure was due to reversal, the separations would certainly have been different in the two cases. The fineness of the fringes with very big plate separations (10 cm.) is a further indication of the absence of reversal.

5. Analysis of Structure.

Since the data for the series $7^1S_0 - m^1P_1$ and $7^3S_1 - m^1P_1$ are more complete than those for $6^1P_1 - m^1S_0$, they will be considered first. The simple term scheme for the lines examined, without showing fine structure, is shown in fig. 3 (a).

It is to be expected that frequency differences which are common to lines involving a common level, will be characteristic of that level. On this basis frequency differences common to the lines $\lambda\lambda$ 6716, 6234 should be characteristic of the 7^1S_0 level. This is, however, not so. The common frequency differences which occur in the four lines are shown in Table VI.

Not all of these are independent and those bracketted together are included as the sum of others. The structure for λ 5676 is the least reliable, and in it the differences *ab*, *bc*, result from three lines of which the centre, *b*, is doubtful. If this is moved by 2 units these differences become 244 and 280 which agree with differences in λ 6072.

Table VI.

λ 6716.		λ 6234.		λ 6072.		λ 5676.	
$7^1S_0 - 8^1P_1.$		$7^1S_0 - 9^1P_1.$		$7^3S_1 - 8^1P_1.$		$7^3S_1 - 9^1P_1.$	
98 <i>ab</i>				99 <i>ef</i>			
244 <i>bd</i>		243 <i>ad</i>		244 <i>ac</i>		246 <i>ab</i>	
157 <i>df</i>		156 <i>bd</i>		156 <i>ce</i>		151 <i>df</i>	
{ 401 <i>bf</i>				{ 400 <i>ae</i>			
{ 490 <i>af</i>				{ 490 <i>af</i>			
122 <i>bc</i>		123 <i>bc</i>		525 <i>ch</i>		121 <i>ef</i>	
= <i>cd</i>				143 <i>df</i>		524 <i>ad</i>	
		32 <i>cd</i>		284 <i>be</i>		145 <i>cd</i>	
						30 <i>de</i>	
						278 <i>bc</i>	

In attempting to set up a scheme of levels which will account for the observed structures, it is usual to accept the recurrence of a particular interval in two lines having a common level as evidence of the existence of this interval within the latter. Adopting this procedure provisionally, it is possible to attribute the differences given below to the levels indicated.

$7^1S_0.$	$8^1P_1.$	$9^1P_1.$	$7^3S_1.$
244	244	244	244
156	156	156	156
122	98	31	525
		122 ?	282
			144

This assumption would mean that the differences 244 and 156 are characteristic of the three singlet levels and also of the triplet level. It is difficult to see how this could come about. A simpler explanation is to assume that these differences are characteristic either of the two $^1P_1$ levels or of the two S levels. It will be seen from fig. 3 (a) that in either case they can appear in the structures of all four lines.

Since the S levels belong to different systems (singlet and triplet) and since their j values are different whilst those of the $^1P_1$ levels are the same, it is more reasonable to assume that these common differences are characteristic of the levels 8^1P_1 and 9^1P_1 and not of the S levels. On this basis the differences could be attributed to the levels as follows :—

$7^1S_0.$	$8^1P_1.$	$9^1P_1.$	$7^3S_1.$
122	244	244	525
	156	156	282
	98	31	144
		122 ?	

There is a doubt about the reality of the 122 value belonging to 9^1P_1 since it has been determined from the component f in $\lambda 5676$, the measurement of

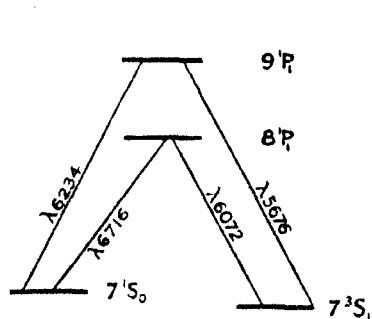


FIG. 3A.—Transitions Investigated.

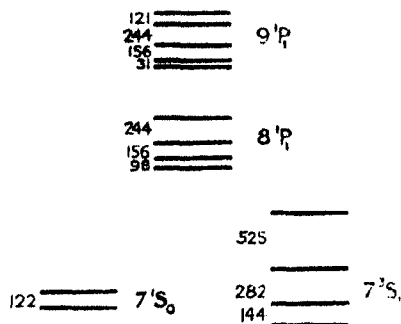


FIG. 3B.—Fine Structure Intervals.

(Scale of Fig. 3B is about 120,000 times that of fig. 3A.)

which is likely to be in error since the separation df is somewhat lower than 156. Whilst it has not yet been found possible to determine the relative positions of the levels themselves, it can be concluded that the 7^1S_0 level is double, the 8^1P_1 level quartet, the 9^1P_1 quartet and possibly quintet and the 7^3S_1 level quartet. The terms may actually be more complex since not all the levels necessarily take part in transitions or show up in common differences.

The nature of the structure is shown in fig. 3B, which is meant to give the number of levels only, the differences being shown merely to indicate their values. Whilst the relative positions are unknown the differences 244, 156, 98 are adjacent to one another in 8^1P_1 , since both the differences 400 and 498 occur, and 244, 156 are adjacent in 9^1P_1 since 400 occurs there too. The transitions have not yet been unambiguously determined, but the usual selection principle apparently does not hold at all. Since there is no reason to doubt its validity, we must conclude that the levels do not all belong to the same atom, but to different isotopes.

Ruark has given a very complex structure for the 6^1P_1 level, finding it to have seven components spaced as follows, 130, 129, 102, 247, 261, 167. A re-examination of the data used by him shows that this is not a necessary conclusion. It has been shown above that a pair of frequency differences is common to two $^1P_1$ levels with different total quantum number. Ruark finds that the lines $6^3P_2 - 7^3D_1$, $6^3P_1 - 7^3D_1$, $6^3P_0 - 7^3D_1$ show the frequency differences 413, 195. He therefore attributes these to the common level 7^3D_1 . He points out that $6^3P_0 - 8^3D_1$ shows the difference 195 and concludes that 8^3D_1 has a structure "somewhat similar" to 7^3D_1 . Further

evidence will be given later as to why approximately equal differences may be expected to recur in terms having the same l and j values. If this is assumed, then Ruark's conclusions as to the structure of the 6^1P_1 level can be modified. Since the differences 247, 261, 167 appear in the lines $6^1P_1 - 7^1D_2$ and $6^1P_1 - 8^1D_2$ he attributes these to the common 6^1P_1 level. But Ruark's data for the line $6^3P_1 - 7^1D_2$ give the difference 263. This is practically identical with the value 261 above and would appear in the three lines only, if it was characteristic of the $^1D_2$ levels. This leaves the values 247 and 167 as belonging to 6^1P_1 . As the value 247 is given by Ruark as the mean of two experimental values 245 and 249, it is seen that this agrees sufficiently well with the value 244 already found common to 8^1P_1 and 9^1P_1 . The other three intervals given by Ruark for 6^1P_1 are got from $6^1P_1 - 7^1D_2$ and $6^1P_1 - 7^3D_2$ which show the differences 130, 129, 102. It may be noticed that 128, 103 also appear in the line $6^1P_1 - 7^3D_2$ and so may equally well be attributed to the 7^3D_2 level as to the 6^1P_1 level. Thus, neglecting this doubtful pair for the present, only 247, 167 and 130 remain as definitely belonging to 6^1P_1 . Further evidence as to the structure of this level can be obtained from the series $6^1P_1 - m^1S_0$ examined here. The differences 55 and 128 are common to $6^1P_1 - 8^1S_0$ and $6^1P_1 - 9^1S_0$, whilst 55 is also found in $6^1P_1 - 10^1S_0$. These could therefore be attributed either to 6^1P_1 or else to the $^1S_0$ levels in general. Since 130 definitely belongs to 6^1P_1 the value 128 found from this series can be identified with this, and as there is no evidence that 55 belongs to the $^1S_0$ levels it can be also attributed to the 6^1P_1 level. It has been shown above that 102 may possibly be attributed to 6^1P_1 , and as the difference 98 occurs in $6^1P_1 - 8^1S_0$ it is probable that these are the same, so that the mean, 100, is likely to belong to 6^1P_1 . The net result is to give the following differences to this level, 244, 167, 128, 100, 55. The differences 244 and 155 ($= 100 + 55$) which are the differences recurring in 8^1P_1 and 9^1P_1 occur in this. There is not enough evidence to determine the structure of 6^1P_1 completely, and it is hoped that a re-investigation of higher members of $6^1P_1 - m^1S_0$ will throw further light on the question.

The differences found here for 7^3S_1 are 525, 282, 144. Of these 282 agrees well with an interval of 281 established by Ruark as belonging definitely to 7^3S_1 . As to 144, differences of 146 and 146, 145 can be obtained from his data for $6^3P_1 - 7^3S_1$ and $6^3P_0 - 7^3S_1$ so that these are no doubt identical with the difference in question; hence 144 may be associated with 7^3S_1 . The difference 519 can also be found in his data, but this is somewhat removed from the value 525 found here.

Before proceeding to the discussion of results a tabulated summary is given below in Table VII for the evidence in favour of common frequency differences belonging to levels of the same l and j value but of different total quantum number. The lines are shown in the first column the differences common to these are shown in the second and the levels to which these differences are attributed on the present interpretation are shown in the third. Some data for cadmium, which will be discussed later, are included below the line.

Table VII.

I.	II.	III.
$7^1S_0 - 8^1P_1$ $7^1S_0 - 9^1P_1$ $6^1P_1 - 7^1D_2$ $6^1P_1 - 8^1D_2$	244, 156	6^1P_1 8^1P_1 9^1P_1
$6^3P_{012} - 7^3D_1$ $6^3P_0 - 8^3D_1$	195	7^3D_1 8^3D_1
$6^1P_1 - 7^1D_2$ $6^1P_1 - 8^1D_2$ $6^3P_1 - 7^1D_2$	261	7^1D_2 8^1D_2
$5^3P_1 - 5^3S_1$ $5^3P_0 - 6^3S_1$ $5^3P_0 - 7^3S_1$	127	5^3S_1 6^3S_1 7^3S_1

6. Discussion of Results.

The origin of fine structure in spectrum lines has been sought, to a certain extent successfully, in the coupling between the optical electron and the spinning nucleus. If i represents the spin quantum number of the nucleus, then a term of given j value will be split into a set of sub-levels, each denoted by a "fine structure quantum number" f , which is obtained by adding i and j vectorially. The number of such levels is $2i + 1$ or $2j + 1$ according to which is the smaller. Transitions to and from these levels are subject to a selection principle which has been found to be* $\Delta f = 0 \pm 1$ ($0 \rightarrow 0$ excluded). On this basis, several fine structures, e.g., Bi, Cd, etc., have been satisfactorily accounted for. The theoretical multiplicity to be expected in the terms of triplet spectra has been worked out by Schüller and Brück† and tested in the

* Schüller and Brück, 'Z. Physik,' vol. 55, p. 575 (1929); White, 'Phys. Rev.,' vol. 34, p. 1397 (1929).

† 'Z. Physik,' vol. 56, p. 291 (1929). This work was examined by Goudsmit ('Naturwiss.,' vol. 17, p. 805 (1929)) who made certain corrections, but supported the main conclusion reached by Schüller and Brück.

cadmium spectrum. All the fine structure can be accounted for by taking $i = \frac{1}{2}$ except for one very strong component in each line. Since the ordinary intensity rule has been found to hold for fine structures, the extreme intensity of these components was a further indication that an origin must be sought for them other than that for the other components. To explain the facts, Schüller and Brück assumed that only the isotopes with odd atomic weight possess an appreciable nuclear spin, and therefore have fine structure levels. Since Aston has shown that the even isotopes are the more abundant in cadmium, the strong lines in the fine structure may be attributed to the even isotopes, thus forming simple triplets without any fine structure. This explanation accounts for all of the components.

Many attempts have been made to explain the mercury fine structures in terms of isotope shift due to a simple mass variation of the Rydberg constant, but these have met with no success, the theoretical shifts being very much smaller than the observed structures. A fine structure, due to mass variation only, has been recently found in the case of neon by various workers,* and since the displacements are of the order predicted there is no reason to expect displacements in mercury, due to this cause, of a quite different order from that predicted. Metcalfe and Venkatesachar,† whilst examining the absorption of the satellites of the green mercury line λ 5461 found that one component was hardly absorbed although there was strong absorption in the others. They suggested that this component may arise from an isotope.

These earlier attempts at analysis did not involve the conception of nuclear spin, and using this as a basis, an attempt will now be made to give a qualitative analysis of the mercury singlet system. Fig. 4 shows the term schemes to be

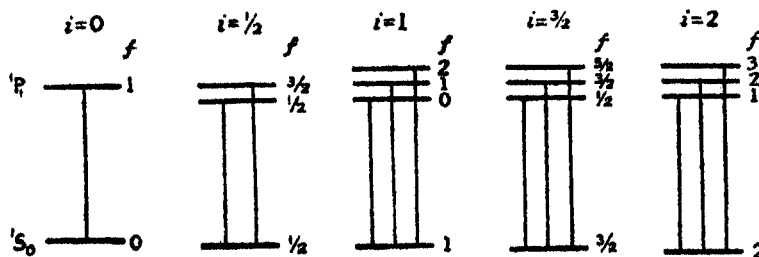


FIG. 4.—Theoretical Fine Structures for $1S_0 - 1P_1$ Series.

* Hansen, 'Naturwiss.', vol. 15, p. 163 (1927); Nagaoka and Mishima, 'Sol. Pap. Inst. Phys. Chem. Res.', Tokyo, vol. 293, p. 13 (1920); Thomas and Evans, 'Phil. Mag.', vol. 10, p. 128 (1930).

† 'Nature', vol. 115, p. 15 (1925); 'Proc. Roy. Soc., A', vol. 105, p. 520 (1924).

expected in the series $7^1S_0 - m^1P_1$ for a number of different values of i . It is seen that in all cases (except $i = \frac{1}{2}$) the number of fine structure components should be three. Since the j value of the 7^1S_0 level is 0 then this level must invariably remain single with $f = i$, and there can never be more than three $^1P_1$ fine structure levels. However it has already been shown experimentally, that the lines are septet, that the 7^1S_0 level is double and that the $^1P_1$ level is at least quartet. There is also evidence that the levels with the same l and j values have common frequency differences. The explanation of these difficulties must be sought for in the isotopic constitution of mercury. These have been recently measured and their abundances accurately determined by Aston.* The values he gives are shown in Table VIII. There are only two isotopes with odd atomic weights and the abundance ratios of even, to the two odd, summing the even, are about 5.1 : 1.2 : 1.

Table VIII.

Atomic weight.	Abundance.	
	Even.	Odd.
196	0.10	—
198	9.89	—
199	—	16.45
200	23.77	—
201	—	13.67
202	29.27	—
204	6.85	—
Total	69.88	30.12

A roughly qualitative explanation of the observed structure can be given by making the following assumptions :—

- (a) The value of i is zero for the even isotopes.
- (b) The value of i is different for the two odd isotopes and in both cases is greater than $\frac{1}{2}$.

These assumptions would give seven components for the structure of a $^1S - ^1P$ line of which the null component, that is, that originating from atoms without nuclear spin, would be much stronger than the rest. The two different values of i would result in two sets of triplets, and this is a possible origin of the doubling of the $^1S_0$ level, and the existence of constant frequency differences

* 'Proc. Roy. Soc.,' A, vol. 126, p. 511 (1930).

in the $^1P_1$ levels. The null line (a in fig. 5) would then be attributed to the even isotopes, the $^1P_1$ and $^1S_0$ levels of which are undisplaced. If one of the

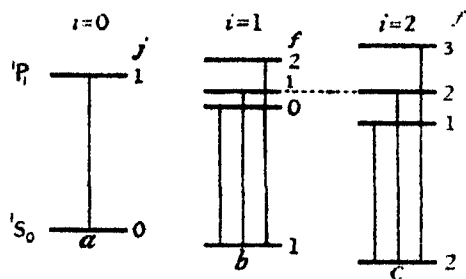


FIG. 5.—Illustrating one possible Origin of a Septet Structure in the $^1S_0 - ^1P_1$ Series, and the apparent Doubling of the $^1S_0$ Level.

isotopes has a nuclear spin with $i \geq 1$ then the corresponding levels will be both displaced, and in addition the upper will be split into three. The amount of displacement will depend entirely upon the coupling of the electron moment with that of the nucleus and therefore on the closeness of approach to the nucleus. With levels of high total quantum number, such as the levels in mercury, the distance of closest approach is practically independent of the total quantum number, with the result that similar displacements occur in terms of the same l and j values, producing frequency differences common to them. It is of interest to note that the 8^1P_1 term is perturbed, as shown by the values of the quantum defect calculated from $7^1S_0 - m^1P_1$ and $6^1S_0 - m^1P_1$. These are :—

6^1P_1	7^1P_1	8^1P_1	9^1P_1	10^1P_1	11^1P_1	12^1P_1
4.10	4.10	3.48	3.90	3.98	4.00	4.01

As shown by Wentzel* this is due to the fact that orbits with lower quantum number just fail to penetrate a closed shell whilst those of higher quantum number succeed in penetrating. The 8^1P_1 level appears to be a border line case, the result being a displacement of the order of $-1,500 \text{ cm.}^{-1}$. It has been shown, however, that this perturbation does not seem to have had any effect on the fine structure, since common differences occur in 6^1P_1 , 8^1P_1 , 9^1P_1 . This is to be expected, for whilst slight penetration of a closed shell has a very marked effect on the term value, because of the alteration in screening constant, the nuclear coupling, being magnetic, is hardly affected by the slight change in distance of the electron to the nucleus, there being no magnetic screening.

* 'Z. Physik.' vol. 19, p. 53 (1923).

Hence although the term is perturbed, the fine structure should remain unchanged.

The same displacement of upper and lower levels of same l and j values but on a different scale, would repeat itself with the second odd isotope. This would result in seven $^1P_1$ and three $^1S_0$ levels, giving a septet structure to the line. If two of the fine structure $^1P_1$ levels coincide, which can happen if the values of i differ by an integer, a frequency difference will result from these levels, which will be common to lines involving both 8^1P_1 and 9^1P_1 levels and this would naturally then be attributed to the $^1S_0$ level. This is shown in fig. 5. A simple illustrative case is worked out for $i = 1$ and 2 (a similar result is got for half integral values if $i > \frac{1}{2}$). The energy differences have been calculated from the formula* $E_{ij} = \frac{1}{2}a \{f(f+1) - j(j+1) - i(i+1)\}$. The difference between the lines bc will repeat with higher $^1P_1$ levels and is the difference in the energy values of the $^1S_0$ terms. It has already been shown that the difference 122 appears to belong to the 7^1S_0 term. The differences 244, 156 which recur in 6^1P_1 , 8^1P_1 , 9^1P_1 are probably the two isotopic displacements. It may be significant that these are approximately in the ratio 3 : 2. Concerning the reality of a constant isotope displacement in terms of the same sequence it may be observed that a similar phenomenon can be found in the experimental data† used by Schüler and Brück for cadmium. In each of the lines $5^3P_1 - 5^3S_1$, $5^3P_0 - 6^3S_1$, $5^3P_0 - 7^3S_1$, the main component, which is attributed to the even isotopes, is displaced by a difference of 127 (not a characteristic of 5^3P_0) from a line of the spin multiplet. This seems to indicate that this difference, known to be an isotope displacement in this case, is a characteristic of the 5^3S_1 , 6^3S_1 and 7^3S_1 levels, which are also levels of reasonably high quantum number (see Table VIII).

Since the abundance ratios of the total even to the odd isotopes are 5.1 : 1.2 : 1, it is to be expected that there should be one line at least ten times stronger than the next intense, this strong line coming from the even isotopes. The observed structures for $7^1S_0 - m^1P_1$ and $7^3S_1 - m^1P_1$ show two lines much stronger than the rest. The series $6^1S_0 - m^1P_1$ should show seven components but $\lambda 4916$ only has five. The great intensity of the main component appears to indicate that this is a fusion of the stronger pair, at least, recorded in the $^1S - ^1P$ series. This fusion may come about by the coincidence of levels.

* Pauling and Goudsmit, "Structure of Line Spectra," 1930.

† Schrammen, 'Ann. Physik,' vol. 83, p. 1161 (1927).

An interesting observation carried out by Jenkins* supports the suggestion made here as to the origin of the fine structures. Jenkins compared the intensities of the satellites of $\lambda\lambda$ 5461, 4358, 4078, 4047 in the spectrum emitted by two samples of mercury of different isotopic content. The two samples differed in atomic weight by 0.18 unit, from which fact he calculated that there was 20 per cent. more of the isotope 198 in the lighter sample than in the heavier, and 27 per cent. more of the isotope 204 in the heavier sample than in the lighter. In spite of this there was no appreciable change in the intensities of the satellites, which at first would seem to indicate that the satellites have not an isotopic origin. However, reference to Table VIII shows that in these two samples, the total amount of even isotopes is practically unchanged, and the odd isotopes are so centrally situated with reference both to the masses and abundances of the others, that very little change in their abundances would take place in the two samples. Hence since the ratios of the total even and the two odd isotopes are practically identical in the two cases, no variation in the intensities of the satellites is to be expected.

The explanation offered here for the structures accounts for most of the difficulties. It gives seven components for the $^1P_1 \leftrightarrow ^1S_0$ series, it accounts for the existence of common frequency differences in a sequence of terms, and it explains the apparent multiplicity of the 7^1S_0 level. There are only two odd isotopes in mercury and two nuclear spins are demanded. The chief outstanding difficulty lies in the fact that there are two strong components in members of the series $7^1S_0 - m^1P_1$ and $7^3S_1 - m^1P_1$ whilst on this view only one would be expected.

Summary.

(1) Fine structures of singlet and intercombination lines in mercury have been investigated in order to obtain information as to the structure of singlet terms.

(2) By the use of a Fabry-Perot interferometer and a high frequency electrodeless discharge at a vapour pressure of 0.001 mm. it is considered that errors due to ghosts and reversal are eliminated.

(3) The following structures have been found:— $7^1S_0 - 8^1P_1$ sextet, $7^1S_0 - 9^1P_1$ septet, $7^3S_1 - 8^1P_1$ octet, $7^3S_1 - 9^1P_1$ septet, $6^1P_1 - 8^1S_0$ quintet, $6^1P_1 - 9^1S_0$ triplet, $6^1P_1 - 10^1S_0$ doublet. Information as to the structures of the 7^1S_0 , 7^3S_1 , 6^1P_1 , 8^1P_1 , 9^1P_1 levels has been obtained

* 'Phys. Rev.', vol. 29, p. 50 (1927).

(4) The structures found for $^1P_1 \leftrightarrow ^1S_0$ lines necessitate more than one value of i and this conclusion is supported by the fact that the $7\ ^1S_0$ level is at least double.

(5) The septet character of $7\ ^1S_0 - 8\ ^1P_1$ can be accounted for by three values of i , one of which is zero, the other two both being greater than $\frac{1}{2}$. The zero value is probably associated with the even isotopes (196, 198, 200, 202, 204) and the other two with the two odd isotopes (199, 201). This is an extension of the suggestion put forward by Schüler and Brück to account for the cadmium fine structures.

(6) The $6\ ^1P_1$, $8\ ^1P_1$, $9\ ^1P_1$ terms, contrary to expectation, show a pair of common frequency differences (ratio 3 : 2). It is shown that similar common differences are obtainable from experimental data given by other workers for mercury and cadmium. These differences, whilst equal in value probably do not involve identical levels but may arise from isotopic level displacements.

I wish to express my deepest thanks to Professor W. E. Curtis for his encouragement and many helpful and valuable suggestions during the progress of the work and the preparation of the paper. This work was done during the tenure of the College Fellowship, Armstrong College, Newcastle-upon-Tyne.

The Elastic Scattering of Slow Electrons in Argon.

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1. *Introduction.*—The failure of classical mechanics to describe adequately the motion of electrons is perhaps best exemplified by the scattering of electrons by various fields of force. The experiments of Davisson and Germer,* G. P. Thomson,† Kikuchi‡ and Rupp,§ in which the scattering of electrons by crystals has been investigated, have shown that diffraction phenomena occur analogous to the diffraction of X-rays. Similarly Rupp|| has shown that electrons may be diffracted by a ruled grating and Mark and Wierl¶ have recently obtained Debye-Scherrer diffraction rings by scattering electrons from heavy molecules. In the latter case the diffraction is due to the symmetry of the molecular structure.

Thus electron scattering analogous to the diffraction of light has been observed in all these cases, but in the scattering of electrons by single atoms no effects analogous to the diffraction of light by small spheres have been obtained. However the investigations of Ramsauer** and others on the total absorbing cross-sections of atoms for slow electrons (2 to 30 volts) have shown that at these velocities a very peculiar variation of cross-section with velocity occurs. In particular for the rare gases a pronounced maximum and a minimum are observed. Now it is to be noticed that at these velocities the electron wave-length is of the order of the atomic diameter estimated classically, so appreciable diffraction effects might be expected. At much higher velocities the maxima and minima would be too close to resolve and the approximate theory of scattering due to Born†† predicts only a regular decrease of scattered intensity with angle for such cases (velocities of the order 100 volts for light

* 'Phys. Rev.,' vol. 30, p. 705 (1927).

† 'Proc. Roy. Soc.,' A, vol. 117, p. 600 (1928), vol. 119, p. 651 (1928).

‡ 'Jap. J. Phys.,' vol. 5, p. 83 (1928).

§ 'Ann. Physik,' vol. 1, p. 801 (1929), vol. 3, p. 497 (1929).

|| 'Z. Physik,' vol. 52, p. 8 (1928).

¶ 'Naturwiss.,' vol. 18, p. 205 (1930).

** *Vide* Kollath, 'Physik Z.,' vol. 31, p. 985 (1930).

†† 'Z. Physik,' vol. 38, p. 803 (1926).

atoms). This has been confirmed experimentally by Dymond.* To detect the maxima and minima it is necessary to investigate the scattering over a large angular range, whereas previous experimental work has been confined to small angles† (up to 60°).

In order to investigate the scattering of slow electrons over a wide angular range and obtain further insight into the Ramsauer effect, experiments have been performed in which the angular distributions of slow electrons (velocities from 4 to 40 volts) scattered elastically in argon, have been measured over an angular range from 15° to 125° . Scattering curves have been obtained showing pronounced maxima and minima, which, at least for the higher voltages, are very similar to those representing the scattering of light by small spheres. It is important to realise, however, that the electron case is much more complicated owing to the great change of electron wave-length in the atomic field and the fact that the field does not fall off discontinuously, so giving no definite atomic radius. Electron exchange phenomena also very much complicate the process.

We now proceed to a more detailed account of the experiments and their interpretation.

2. *Description of the Apparatus.*—The apparatus was similar to that used by Arnot (*loc. cit.*). Electrons from a plain tungsten filament A (fig. 1A) were accelerated through a pair of slits B (4×1.5 mm.) and C (2×0.6 mm.), 7 mm. apart, into an electrostatically shielded space containing gas at a few thousandths of a millimetre pressure. Electrons scattered in the region D could be collected by a Faraday cylinder E enclosed in a case carrying two slits F and G (2×0.6 mm.), 6 mm. apart, the front one being 7 mm. from the axis. The gun and Faraday cylinder were both carried on the same 4 cm. ground joint H, the Faraday cylinder being rotated on a 1 cm. ground joint J coaxial with this. This construction enabled the slits to be aligned on the axis of rotation of the Faraday cylinder before assembling the joint H. The gun and Faraday cylinder were made from copper foil, the joints being spot-welded together. The supports were of "Staybrite" steel in its non-magnetic state. The scattering space was enclosed by a copper shield K, the whole system being contained in a Pyrex bulb.

Fig. 1B gives a diagrammatic representation of the geometrical arrangement of electron source and collector. It shows that the angular range of collection

* 'Proc. Roy. Soc.,' A, vol. 122, p. 571 (1929).

† Arnot, 'Proc. Roy. Soc.,' A, vol. 25, p. 660 (1929); Harnwell, 'Phys. Rev.,' vol. 34, p. 661 (1929); Macmillan, 'Phys. Rev.,' vol. 36, p. 1034 (1930).

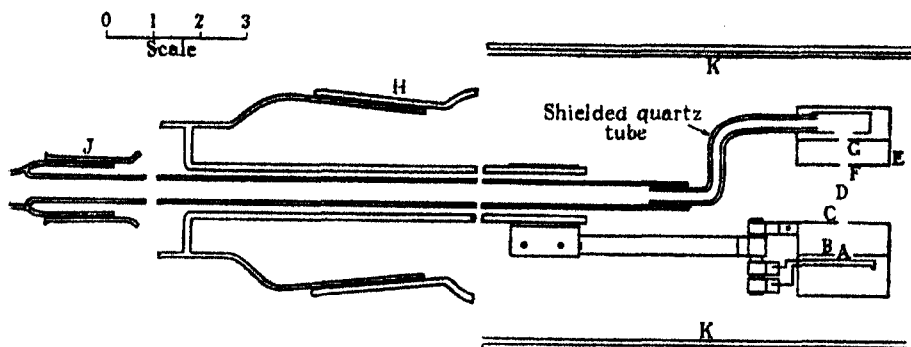


FIG. 1A.—Diagrammatic Section of Apparatus.

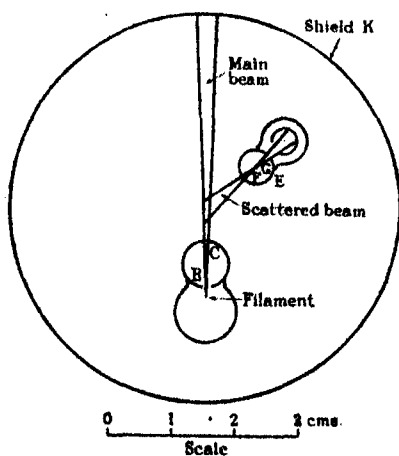


FIG. 1B.—Illustrating method of Experiment.

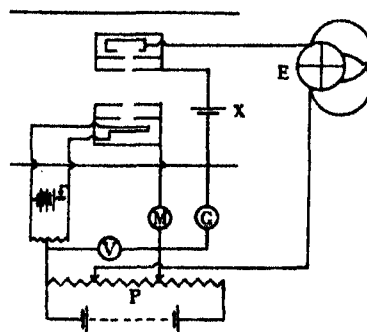


FIG. 1C.—Electrical Connections.

is about 10° though the actual range cannot be determined from purely geometrical considerations depending as it does on width and diffuseness of the main beam, etc.

The electrical connections are shown in fig. 1c. Accelerating and retarding potentials could be applied between the collector and its case by a potential divider P. The total emission from the filament was measured by a milliammeter M, the current leaving the gun by a galvanometer G, and that collected by the Faraday cylinder by the rate of deflection of the electrometer E. The potential between the filament and the case of the gun was measured by a voltmeter V. X is a dry cell which was used to prevent the collection of positive ions, when working above the ionisation potential.

A continuous flow of gas could be maintained through the apparatus, the gas entering through a very fine leak and being pumped away through a short

length of capillary. The pressure in the tube was measured by a McLeod gauge, and could be varied by varying the pressure in the reservoir. The argon was supplied by the British Oxygen Company as 99 per cent. pure, and was not further purified.

It was found essential to bake the tube at about 400°C . on pumping down after admitting air. Without this precaution the current collected by the Faraday cylinder without gas in the apparatus was comparable to that scattered by the gas and no reproducible results could be obtained. The rest of the glass work was baked with a Bunsen burner.

3. *Checks on the Working of the Apparatus.*—It is necessary to show that the current collected by the Faraday cylinder consists of electrons scattered by the gas from the main electron beam and retaining all their energy. The following tests show this to be so :—

(a) With no gas in the apparatus the current collected was barely measurable except within 10° on each side of the main beam, and was never more than a few per cent. of that obtained with gas present at a pressure of a thousandth of a millimetre.

(b) The collected current was proportional to the total current leaving the gun. Special attention was paid to this point and tests were made which showed the collected current to be accurately proportional to the total current in the main electron beam. Alterations in the gun reducing the stray current escaping through holes by a factor of 10, produced no difference in the results. The collected current is therefore derived from the main beam.

(c) Except near the main beam, the collected current was proportional to the pressure over the range of pressures (1 to 2×10^{-3} mm. Hg) used as is shown in fig. 2. It is therefore the result of single scattering in the gas. At angles below 40° there was a departure from proportionality for pressures above 3×10^{-3} mm. Hg which is probably due to the onset of multiple scatter-

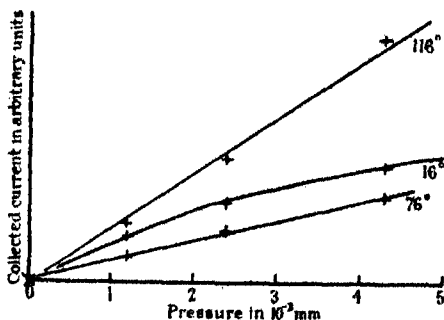


FIG. 2.—Illustrating dependence of scattered current on pressure at 8 volts.

ing. This would be expected at about this pressure, for the mean free path at 8 volts as determined by Ramsauer (*loc. cit.*) is about 5 cm. at 3×10^{-3} mm. Hg, and 20 per cent. of the electrons which would have been collected will therefore be deflected through an angle greater than the critical angle in Ramsauer's experiments. The proportion deflected through angles large enough to prevent collection will be rather less than this.

(d) Retarding potential curves obtained by applying a retarding potential between the collector and its case showed the collected current to consist of two parts:—

- (1) A fairly homogeneous group having the full energy of the incident beam.
- (2) Electrons which have lost 25 to 100 per cent. of their energy. The latter, which were partly due to scattering of the main beam by shields and slits and partly to inelastic collisions with argon atoms, could be eliminated by a retarding potential of about 80 per cent. of the energy of the incident electrons.

Examples of the retarding potential curves obtained are shown in fig. 3;

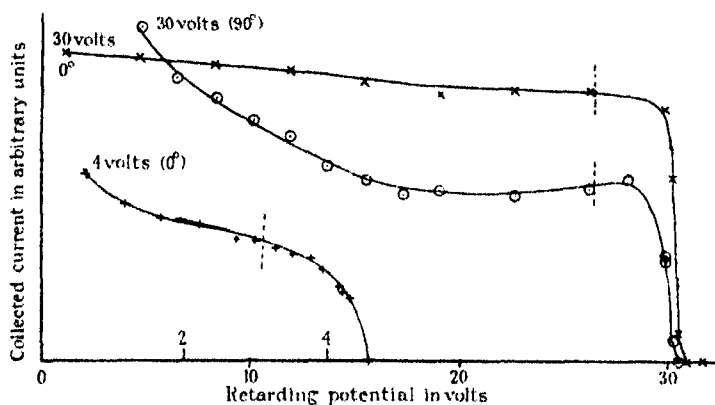


FIG. 3.—Retarding potential curves. Dotted line indicates retarding potential used in experiment.

the vertical dotted line shows the retarding potential used in the angular distribution investigation at the corresponding voltage. The absence of any kink due to the 11.6 volt resonance potential in argon is probably due to this level being metastable and so appreciably excited only by voltages very close to the excitation potential. This has been found experimentally by various authors* and predicted theoretically by Oppenheimer.†

* E. G. Dymond, 'Proc. Roy. Soc.,' A, vol. 107, p. 291 (1925); W. C. Michels, 'Phys. Rev.,' vol. 36, p. 1362 (1930).

† 'Phys. Rev.,' vol. 32, p. 361 (1928).

It will be noticed that the retarding potential curves for 30-volt electron exhibit the peculiarity that the collected current in the region of 20 volts retarding potential appears to fall off with diminishing retarding potentials. This is due to secondary electron emission from the Faraday cylinder. The effect could doubtless be removed by the use of a more complicated Faraday cylinder, but for the present purpose this is not necessary as only the elastic scattering is being studied.*

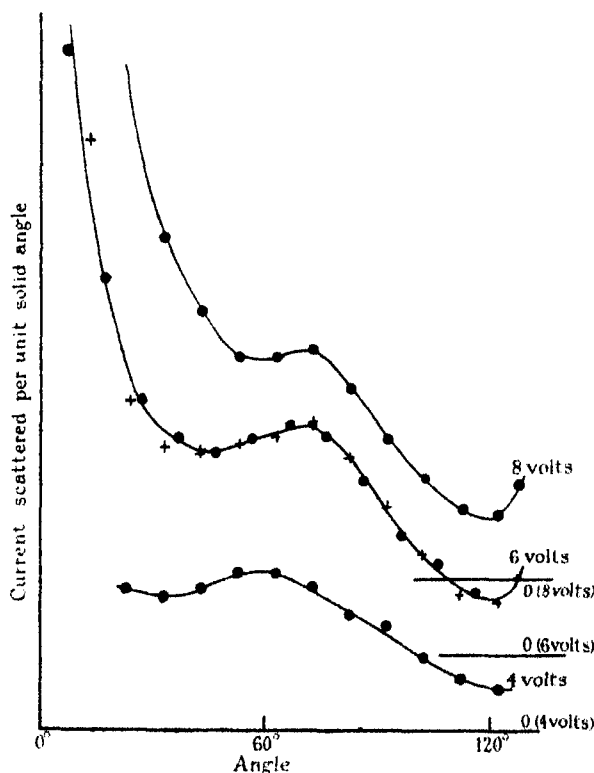


FIG. 4.—Scattering curves for 8, 6 and 4 volts.

(e) When the energy of the incident electrons was above the ionisation potential there was a large positive ion current to the collector, which at big angles was greater than the electron current. These ions could be completely stopped by a small positive potential applied to the case of the collector. This was tested by applying a retarding potential between the case and collector to stop electrons reaching the latter. Any positive ion current could then be

* As it is clear that the electron beam is not very homogeneous at 4 volts, no great accuracy can be claimed for the scattering curves for such electrons, but the general form of the curves obtained is believed to be correct.

readily detected. By experiments below the ionisation potential, with and without the battery X (fig. 1c), this battery was found to have no appreciable effect on the results. Actually 0.9 volt was used below 35 volts, and 4.5 above.

In order to determine the true accelerating voltage applied to the electron beam the ionisation potential of the gas was measured. This was done by arranging the conditions to be the best possible for the collection of positive

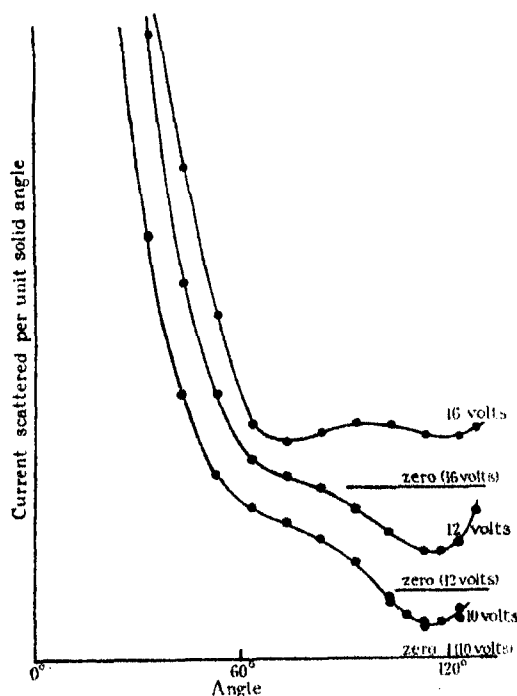


FIG. 5.—Scattering curves for 16, 12 and 10 volts.

ions undisturbed by electrons. A retarding potential was applied between the case and collector to prevent the collection of electrons while the battery X was reversed, so applying a small negative potential to the collector case and facilitating the collection of positive ions. The experiment was performed with the Faraday cylinder set at 90° , as at this angle the positive ion current, owing to space charge effects, is a maximum.* The accelerating voltage of the main beam electrons was then varied until a positive ion current was received by the Faraday cylinder. A value of 15.5 ± 0.2 volt was obtained, agreeing well with the accepted value of 15.6 volts. This shows the contact

* *Vide* F. L. Arnot, 'Proc. Roy. Soc.,' A, vol. 129, p. 361 (1930).

potential between the filament and gun slits to be less than half a volt and so insufficient to disturb the voltage scale.

4. *Results.*—To investigate the angular distribution, the retarding potential was chosen so that only elastically reflected electrons were collected and readings of the current to the collector taken at 10° intervals. The beam used varied from 10^{-6} to 10^{-8} amperes according to the angle and velocity under investigation. The collected currents were of the order 10^{-12} amperes. The readings were reduced to a standard pressure and current in the beam, and the angular zero determined from the symmetry of the resulting plot. To obtain the true relative scattering per unit solid angle it is necessary to multiply the readings by the sine of the angle of scattering in order to allow for the variation in the volume of the space from which electrons can be scattered from the beam into the collector (see fig. 1B).

Examples of the curves so obtained are given in figs. 4, 5 and 6. For 6 volts points obtained on both sides of the main beam are given, exhibiting the symmetry. Table I gives the data from which figs. 7, 8 and 9 are plotted.

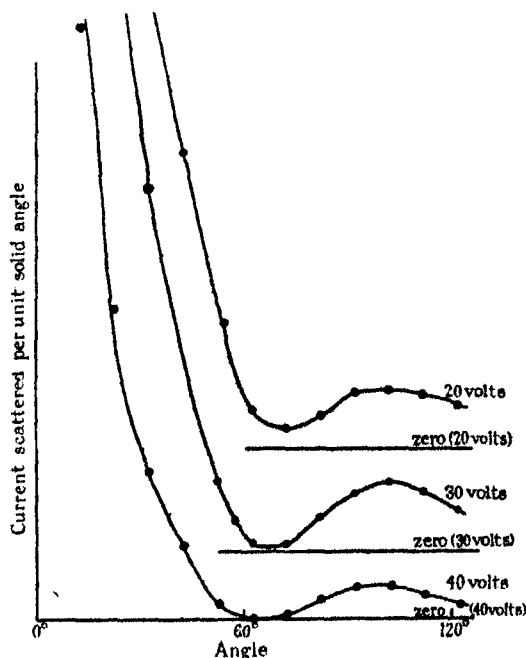


FIG. 6.—Scattering curves for 20, 30 and 40 volts.

The curves all refer to the same beam and pressure and are comparable if the effective collecting area of a slit is assumed independent of velocity.*

* Owing to lack of space some of the experimental results obtained for small angle scattering are not plotted in the diagrams.

Table I.

Angle Volts	13°	23°	33°	43°	53°	63°	73°	83°	93°	103°	113°	123°	128°
40	86	45	21	10.7	2.5	0.18	0.95	3.0	4.55	4.8	3.6	2.2	—
30	156	92	53	25	19	1.6	1.3	5.0	8.6	10.4	8.9	6.2	—
20	133	90	77	43	18	5.6	3.0	4.9	8.1	8.5	7.9	6.3	—
16	190	140	87	46	25	9.3	6.5	7.9	9.5	9.1	7.8	7.6	8.9
12	170	120	81	45	29	19	17	15	12	8.8	5.8	7.6	12
10	137	105	63	39	27	22	20	7.7	14.3	8.8	5.1	6.7	—
8	520	270	78	52	38	34	32	25	19	14	10	11	16
6	69	33	28	27	28	29	31	27	20	14	8.4	7.7	10.4
4	—	20	19	20	22	22	20	17	15	11	8	6.6	—

As has been observed by the other workers, at the higher voltages there is a rapid fall of scattered intensity with increasing angle at small angles. This fall becomes less rapid at the lower voltages as would be expected on general grounds. However the most interesting features of the results appear at large angles. In all cases maxima and minima are observed, the positions and magnitudes of which vary steadily with the velocity of the incident electrons.

To obtain the total scattering per unit angle the results of figs. 4, 5 and 6 must be again multiplied by the sine of the angle of scattering. Some of the results so obtained are shown in fig. 7. The curves have been extrapolated to

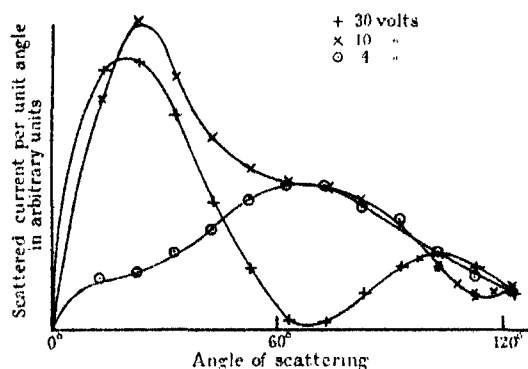


FIG. 7.—Illustrating variation of cross section with velocity. Areas of curves proportional to total cross section at velocity indicated.

pass through the origin. By integrating these curves we may get the total scattering between any two angles; the total scattering in the range 0° to 120° calculated in this way is shown in fig. 8.

Ramsauer and others (*loc. cit.*) have studied the total scattering as a function of the velocity. Ramsauer's curve for argon is shown in fig. 8 for comparison.

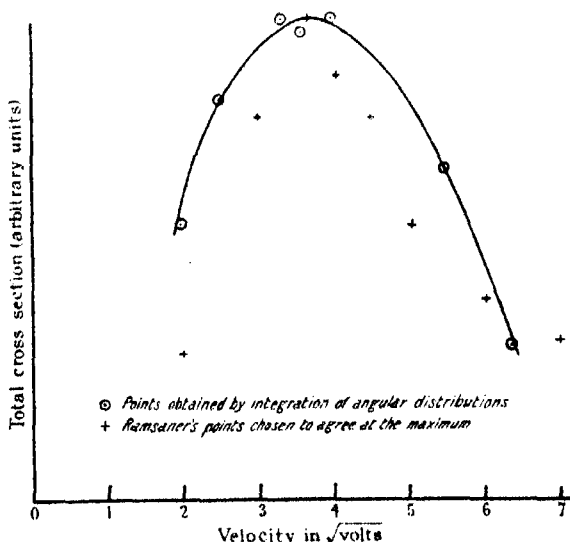


FIG. 8.—Total cross sections obtained by integration of angular scattering curves.

There is a general similarity between this and our 0° to 120° curve. Exact agreement would not be expected since—

- (1) We have not included electrons scattered between 120° and 180° ;
- (2) There is some uncertainty about the extrapolation to zero angle of scattering ;
- (3) Ramsauer's curve includes electrons scattered inelastically ;
- (4) We have assumed the effective collecting area of a slit to be independent of velocity of the incident electrons.

From fig. 7 it may be clearly seen that the reason for the maximum cross section observed at 13 volts is that electrons of higher velocity are scattered to a less extent at large angles while those of smaller velocity are scattered less at small angles.

5. *Discussion.*—It will be seen that the higher voltage curves exhibit general similarity to those representing the intensity of light scattering from small spheres. That this analogy may be of some significance can be seen from the fact that the argon atom is spherically symmetrical and has a field of force with a relatively sharp boundary. That the electron wave-lengths used (of the order 2 Å.U.) are comparable with the radius of the argon atom (2.6 Å.U.)

also fits in with this. However, the analogy must not be pushed too far as the electron wave-length varies very rapidly in the region of the atom thus rendering necessary a more detailed treatment.

The simplest method of treating scattering in quantum mechanics is due to Born.* This theory virtually assumes the distortion of the incident wave by the scattering field to be small and as a consequence is not valid for low velocities. The theory has to be extended in several directions, viz. :—

- (a) To obtain correct formulæ for the scattering of slow electrons by a static field.
- (b) To allow for interchange between atomic and colliding electrons.
- (c) To include the distortion of the atomic field due to the colliding electrons, i.e., polarisation and inelastic collisions. The complete theory must include interaction between elastic and inelastic collisions.

Faxen and Holtsmark† have developed a method of treating the first of these. The method is tedious to work out and leads to an oscillating series for the angular distribution. However, Holtsmark‡ has successfully calculated the total cross sections for argon, and in later unpublished work, which he has kindly communicated to us, has made preliminary calculations of the angular distributions for 6, 12 and 30 volt electrons. These agree well with our experimental curves, but owing to the slow convergence of the series too much reliance cannot be placed on this agreement until the calculations have been extended.

The effect of electron exchange has been considered by Oppenheimer§ in a qualitative way, and he shows that for closed shells maxima and minima might be expected due to interference of the electron waves representing the scattered incident particle and electrons ejected by interchange from the atom. Such interference effects occur in the scattering of α -particles by helium.|| As Oppenheimer's theory can be worked out for simple atoms only, it is necessary to extend the above experiments to helium to distinguish Oppenheimer's theory from Faxen and Holtsmark's as an explanation of the angular distributions.

* 'Z. Physik,' vol. 38, p. 803 (1926).

† 'Z. Physik,' vol. 45, p. 307 (1927).

‡ 'Z. Physik,' vol. 55, p. 437 (1928).

§ 'Phys. Rev.,' vol. 32, p. 361 (1928).

|| N. Mott, 'Proc. Roy. Soc.,' A, vol. 126, p. 259 (1930); Chadwick, 'Proc. Roy. Soc.,' A, vol. 128, p. 114 (1930); Blackett and Champion, 'Proc. Roy. Soc.,' A, vol. 130, p. 380 (1931).

With regard to polarisation, Holtsmark* has taken it into account in an approximate manner by modifying the static field used. As the polarisation will almost certainly increase with decrease of velocity this will affect the 6-volt curve to a greater extent than the higher voltage ones and due allowance must be made for this in any theory.

It is clear that much remains to be done in order to understand the above phenomena completely, and the work is to be extended to larger angles, higher velocities (to ascertain when the peaks disappear) and to other gases (in particular the other rare gases). Further theoretical calculations are in progress also.

In conclusion we wish to express our indebtedness to Sir Ernest Rutherford for his advice and encouragement and also to Mr. P. M. S. Blackett and Dr. M. L. E. Oliphant for much discussion and many valuable suggestions. One of us (E.C.B.) is indebted to the Department of Scientific and Industrial Research for a grant.

Summary.

The angular distribution of slow electrons scattered elastically in argon has been investigated over a wide angular range (from 15° to 125°). Scattering curves have been obtained for 4, 6, 8, 10, 12, 16, 20, 30 and 40 volt electrons. All exhibit maxima and minima analogous to those occurring in the scattering of light by small spherical obstacles. These results are described and their bearing on the Ramsauer effect and the quantum theory of scattering discussed.

* 'Z. Physik,' vol. 52, p. 485 (1929).

*The Photosensitised Decomposition of Nitrogen Trichloride.—
Part I.*

By JOHN G. A. GRIFFITHS and RONALD G. W. NORRISH.

(Communicated by T. M. Lowry, F.R.S.—Received December 12, 1930.)

The present work is introductory to a detailed study of the nature of the induction period of the photochemical reaction between hydrogen and chlorine. Whatever the mechanism finally adopted for this process, it is essential that it should admit of a clear interpretation of the remarkable inhibition exerted by small traces of ammonia or nitrogen trichloride; conversely, if the full details of this inhibition be thoroughly understood there seems a possibility that they will yield valuable evidence as to the nature of the photochemical union of hydrogen and chlorine.

As is well known Burgess and Chapman* traced the cause of the induction period to the existence of ammoniacal impurities in the water of the actinometer, and by special purification they were able to eliminate the inhibition almost completely; further, artificial induction periods were produced by the addition of small quantities of ammonia solution to the actinometer. The intense nature of the inhibition is shown by an interesting calculation of Chapman,† who shows that one part of nitrogen trichloride in 10^6 parts of hydrogen and chlorine cuts down the rate of formation of hydrogen chloride by 100 times. By a different technique, in which water was eliminated from the reaction system, Norrish‡ discovered that the length of the induction period is directly proportional to the weight of ammonia added to the reaction mixture of hydrogen and chlorine, and the sharpness of the onset of the photochemical reaction at the end of the period of induction is well characterised by the Draper effect, as shown in one of his curves which is reproduced in fig. 1.

Chapman and McMahon§ pointed out that chlorine reacts with ammonia to produce nitrogen trichloride, and they found that this substance was one of the most effective inhibitors. There is little doubt therefore that the action of ammonia is due to the subsequent formation of nitrogen trichloride when it is

* 'J. Chem. Soc.,' vol. 89, p. 1399 (1906).

† 'Science Progress,' vol. 7, p. 72 (1912).

‡ 'J. Chem. Soc.,' vol. 127, p. 2323 (1925).

§ 'J. Chem. Soc.,' vol. 95, p. 1717 (1909); vol. 97, p. 847 (1910).

mixed with the chlorine, a conclusion which is fully borne out by the results of the present investigation.

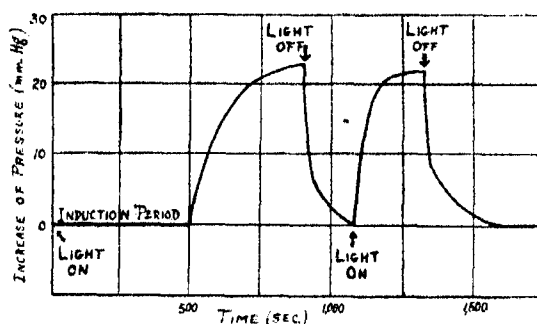


FIG. 1.

In our preliminary experiments, using a modification of the technique employed by Norrish (*loc. cit.*), it was observed that a small continuous rise of pressure occurred during the period of inhibition (fig. 2). This change is

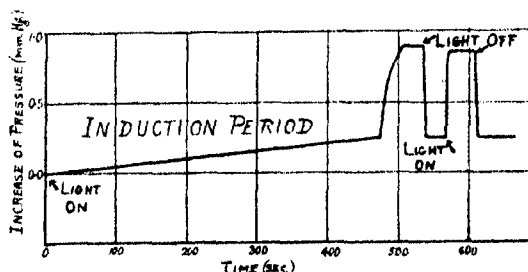
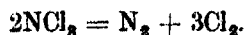


FIG. 2.

definitely distinct from the almost instantaneous small rise of pressure (Budde effect) which occurs when chlorine is first illuminated and also from the larger increase of pressure (Draper effect) which marks the conclusion to the induction period.* The effect was attributed to the decomposition of the nitrogen trichloride during the induction period, according to the equation



* The difference in magnitude of the Draper effects recorded in the two figures is due to the much greater light intensity used in the earlier work where the full light of the mercury vapour lamp placed close to the reaction vessel was employed. The original pressure gauge was much less sensitive than that used in the present work, and this accounts for the failure to observe the small increase of pressure during the induction period.

Subsequent results, as will appear, have fully confirmed this view and exclude any possibility of connecting the induction period with the presence of dry ammonium chloride. This is in accord with the result of Noyes and Haw* who found that dry chlorine and dry ammonium chloride do not interact.

It was subsequently found that regular pressure increases of exactly the same magnitude were obtained when the hydrogen was omitted from the reaction system, and the speed with which they were attained was directly proportional to the quantity of light absorbed by the chlorine. We thus have to deal with a photochemical reaction sensitised by chlorine. Experiments indicated that the region of photochemical activity was confined to the blue and ultra-violet parts of the spectrum since no effect was observed with yellow (579 $\mu\mu$) or green (546 $\mu\mu$) light. In addition the change obeys with remarkable fidelity a zero molecular law with respect to the nitrogen trichloride. The final stage of the reaction was marked by an almost explosive increase of pressure, followed by an equally rapid decrease, after which the pressure remained constant (see fig. 5, p. 602). This semi-explosive termination of the reaction constitutes one of its most puzzling features; it is more marked and distinct at low total pressures than at high, while its magnitude seems at least qualitatively to be proportional to the intensity of the light.

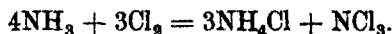
Measurements of the quantum efficiency with homogeneous light of wavelengths 365 and 436 $\mu\mu$ were made, the values obtained depending markedly on the total pressure of chlorine. At low pressures as many as 20 molecules of nitrogen trichloride were decomposed per quantum, while at high pressures the efficiency fell to a limiting value in the neighbourhood of 2. The decomposition thus apparently occurs by way of a chain reaction, the length of the reaction chains being limited by the total pressure of chlorine in the system. In Part II the study has been extended to include the effect of "inert" gases, with analogous results, the bearing of which will be considered later.

*The Formation of Nitrogen Trichloride from Chlorine
and Ammonia.*

The mixtures of chlorine and nitrogen trichloride were prepared by rapidly adding excess of dry chlorine to dry gaseous ammonia in a mixing chamber from which all light was excluded. Under these conditions a cloud of ammonium chloride was formed which settled out on the walls of the vessel, and the resulting mixture of chlorine and nitrogen trichloride could be stored for a period of several days without much decomposition. The ideal equation for the reaction

* 'J. Amer. Chem. Soc.,' vol. 42, p. 2187 (1920).

is given by Noyes and Haw (*loc. cit.*), who showed that when anhydrous ammonia and chlorine interact at -90° C. three molecules of ammonium chloride are formed for every four molecules of ammonia employed :



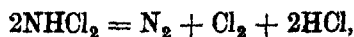
It is necessary to examine in detail the validity of this equation.

Under the conditions of mixing the dry gases at atmospheric temperature we generally found a small deficiency of nitrogen chloride, pointing to its partial decomposition. Further if more than a limiting pressure of *ca.* 25 mm. of ammonia was used, the mixing of the gases was accompanied by a sharp click, and no nitrogen trichloride was obtained, although the usual cloud of ammonium chloride was produced. A similar result was obtained if the order of mixing was reversed and the ammonia gas added to the chlorine ; here again ammonium chloride was deposited but no nitrogen trichloride was formed, and chlorine so treated showed no induction period when mixed with hydrogen and irradiated. It seems clear that when the gaseous concentration of the nitrogen trichloride exceeds a certain limit during its formation, it explodes to give a mixture of chlorine and nitrogen, products which, of course, would not effect the inhibition of the hydrogen-chlorine reaction



That the product obtained was nitrogen trichloride and not other chlorinated ammonias is supported by the work of Gattermann,* who showed that when partially chlorinated ammonias are produced by the action of chlorine on solutions of ammonia or ammonium chloride they are decomposed by excess of chlorine into nitrogen chloride and ammonium chloride, and since in our work the ratio of chlorine to ammonia was never less than 80 : 24 and usually many times greater, this condition was amply fulfilled. In addition to the work of Noyes and Haw cited above we also have the observations of Marckwald and Wille† who found that dry chloroamine (NH_2Cl) decomposes at so low a temperature as -50° into nitrogen, chlorine, nitrogen trichloride, and ammonium chloride.

The evidence from other investigations did not, however, completely exclude the possibility that the observed effects might be due to dichloroamine which might be supposed to decompose in light according to the equation :



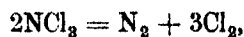
or in some other reaction involving the production of ammonium chloride.

* 'Ber. Deuts. Chem. Ges.,' vol. 21, p. 751 (1888).

† 'Ber. Deuts. Chem. Ges.,' vol. 56, p. 1319 (1923).

This possibility is, nevertheless, ruled out by the fact that no acidity could be found in the gaseous products of irradiation, although the method used was easily sensitive to the detection of 2×10^{-7} g. mol. of hydrogen chloride.* In addition, no traces of ammonium chloride were produced on the walls of the photo-reaction vessel as a result of the photo-decomposition.

Since, therefore, nitrogen trichloride is the only chlorinated ammonia obtained by adding excess of chlorine to dry ammonia at room temperature, one-half of the increase of pressure resulting from irradiation of the resulting mixture should be due to the production of nitrogen according to the reaction,



and, also, any observed deficiency in the yield of nitrogen chloride, calculated from the equation of Noyes and Haw, should be represented by nitrogen produced in accordance with the above equation.

These conclusions were verified by the observation that the mixture of nitrogen trichloride and chlorine contained, before irradiation, a small quantity of a gas (nitrogen) which could not be condensed in a small side tube of the reaction vessel by means of liquid air, and the pressure of this gas was very nearly that which would be expected if the observed deficiency of nitrogen trichloride was due to decomposition during preparation. Moreover, one-half of the increase of pressure, developed during the irradiation experiments, was found to be due to a gas (nitrogen) which could not be condensed in liquid air.

As an example, in one experiment, 74.6 mm. of reactive mixture, 3 days after preparation, and calculated, by means of the equation of Noyes and Haw, to contain 0.945 mm. of nitrogen trichloride, contained 0.325 mm. of nitrogen, and on illumination of the mixture the pressure increased by 0.40 mm., of which almost half, 0.21 mm., was due to nitrogen. Therefore, in the 3 days $(0.945 - 0.40) = 0.545$ mm. of nitrogen trichloride had decomposed. This should have yielded 0.273 mm. of nitrogen. The observed value was 0.325 mm., which is satisfactory in view of the experimental difficulties.

It may therefore be stated definitely, in view of this additional evidence,

* The determination of small quantities of hydrogen chloride in the presence of chlorine was carried out by evacuating the reaction vessel through a tube cooled in liquid air whereby the chlorine and hydrogen chloride were frozen out. The condensate was then treated with excess of potassium iodide and the iodine liberated was exactly titrated with sodium thiosulphate, starch being the indicator. Any residual acidity could then be determined by estimating the iodine set free on adding excess of potassium iodate. Treadwell and Hall, 'Analytical Chemistry,' p. 670 (1919).

that nitrogen trichloride is the only chlorinated ammonia obtained by adding excess of chlorine to ammonia under our experimental conditions.

EXPERIMENTAL.

A general plan of the apparatus used is shown in fig. 3. Pure dry ammonia gas was stored in the globe A over quicklime, its total pressure being registered by the mercury manometer M_2 . Chlorine was stored in a liquid air trap, and could be admitted by the tap N_1 . The mixing of chlorine and ammonia was

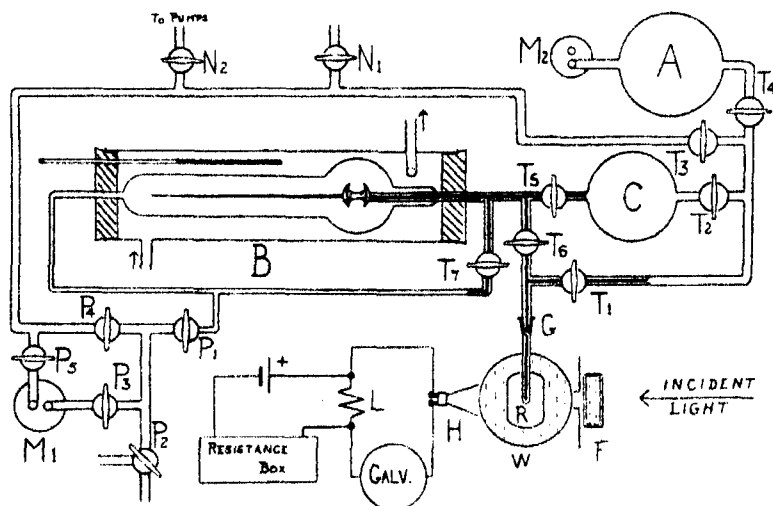


FIG. 3.

carried out in the mixing chamber C, and the chlorine charged with nitrogen trichloride was stored there till required. Irradiation was carried out in the reaction vessel R—a flattened bulb of 75 c.c. capacity and with approximately plane faces—situated in the light beam furnished by the optical system described below.

This technique eliminated the deposition of the ammonium chloride on the walls of the photo-reaction vessel, R, where such a substance would interfere with the measurement of the intensity of light transmitted by the vessel and received on the face of the thermopile, H.

Total pressures in C and R, and also the small pressure changes in R due to irradiation, were measured by means of the Bourdon gauge B, which was connected with the reaction vessel R by way of the ground glass joint G and capillary tubing of 1 mm. bore. The temperature of the gauge and the reaction vessel was regulated to $25^\circ \pm 0.01^\circ \text{C}$. by pumping water from an

electrically controlled thermostat to a cistern with a constant level device; from this the water flowed back to the thermostat in two streams, one through the outer jacket of the gauge, and the other through the glass tank W which served as a bath for the reaction vessel. The apparatus could be evacuated by a water pump or the "hyvac" pump via N_2 .

The Bourdon gauge was used in conjunction with a travelling microscope by means of which deflections of the pointer could be read, giving an accuracy in the measurement of small changes of pressure of 0.002 mm. Hg. The gauge was calibrated against a mercury manometer as described by Norrish (*loc. cit.*). Its deflection was found to be linear over a range of pressures of 10 mm. In using the instrument by the null method, the pressure of air in the outer jacket was controlled by the tap P_2 which communicated both with the atmosphere and a filter pump through appropriate drying tubes, the total pressure being read on the vertical mercury manometer M_1 .

Materials.

Chlorine was prepared by the interaction of pure hydrochloric acid and potassium permanganate. The gas was washed with water, dried with phosphoric oxide and was then collected and stored in a liquid air trap. Since liquid chlorine dissolves air, the first fraction was allowed to boil off under vacuum until the yellow liquid ceased to bump.

Ammonia was prepared by warming recrystallised A.R. grade ammonium chloride with pure sodium hydroxide solution. The gas was dried with soda lime and collected in a liquid air trap. The ammonia was allowed to evaporate slowly, and the middle fraction was collected for storage in the previously evacuated litre globe, A, to which was attached a bulb of quicklime. Analysis of a sample of the gas showed that it contained less than 0.1 per cent. of gases unabsorbable by hydrochloric acid, and moreover, at a pressure of 100 mm. the ammonia did not react with phosphoric oxide.

Preparation and Storage of Mixtures of Nitrogen Trichloride and Chlorine.

In the technique finally adopted, 15 to 24 mm. of ammonia were admitted to the previously evacuated store vessel C, of about 200 c.c. capacity, via taps T_4 and T_3 , the Bourdon gauge being used as a null instrument. The ammonia in the connecting tubes between taps T_3 and T_4 was then pumped out via T_3 and N_2 , tap T_5 was closed, and N_1 and T_3 were opened. The chlorine was next allowed to warm up until its vapour pressure was about 100 mm., tap T_2 was then opened for 2-3 seconds so that gas entered the globe C with

a rush. (The yield of nitrogen chloride was found to be low if the chlorine was added slowly.) Tap T_5 was opened cautiously and air was admitted to the outer part of gauge B to balance the pressure of the chlorine in C. More chlorine, as desired, was then added slowly to C, via tap T_2 . The inner and outer parts of the gauge and the connecting tube were then evacuated completely through P_1 , P_4 and N_2 .

It was noticed that all of the nitrogen trichloride from a preparation was decomposed in the course of 24 hours when the store vessel C was clean, but when the inside had become coated with solid ammonium chloride after several preparations the nitrogen trichloride persisted for as long as a week. It was further found, contrary to our expectations based on the conclusions of previous investigations,* that the mixtures of nitrogen trichloride and chlorine could be passed through taps lubricated with rubber-free vacuum grease without appreciable decomposition of the chloride. It seems probable that slight chlorination of the tap grease decreases its power of decomposing the nitrogen trichloride, and further that the great dilution of the latter by chlorine so lowers its speed of diffusion to the grease as to confer a large measure of protection.

The Optical System.

The source of light was a 3000-c.p. quartz mercury vapour lamp run at a constant burner voltage of 150 volts from a storage battery of 220 volts and consuming a current of 4 amps. Under these conditions, the intensity of the light did not vary by more than 1.5 per cent. from the mean during the course of the day. The radiation was brought into a narrow beam by means of a system of lenses and stops and then passed through the reaction vessel R (fig. 3), finally being focussed so that nearly the whole of the light field fell directly on the blackened face of a Moll thermopile (H), the rest being reflected on to the elements by the conical reflector (see below). The intensity of the radiation was controlled by the iris diaphragm in the screen immediately in front of the lamp.

Homogeneous radiations of wave-lengths $365\text{ }\mu\mu$ and $436\text{ }\mu\mu$ were obtained by placing the appropriate colour filters described by Norrish† in the path of the light at F (fig. 3), the heat rays being excluded by a layer of 6 per cent. copper sulphate solution, 3 cm. thick.

The thermopile (H) was connected with a Broca galvanometer of resistance

* e.g. Porret, 'Nicholson's J.', vol. 34, pp. 180, 276 (1813).

† 'J. Chem. Soc.', p. 1158 (1929).

50.5 ohms, a soft iron cylinder being used to shield the galvanometer from external magnetic fields.

During the course of the day, the zero of the galvanometer changed considerably. This effect was eventually traced to the variation of E.M.F. generated owing to the back of the thermopile being at room temperature, which gradually increased, and the funnel being at an approximately constant temperature as a result of proximity to the water jacket W. The E.M.F. was counterbalanced by including in the galvanometer circuit a small variable potential difference provided by means of a copper wire, L, fig. 3, of low resistance. This wire was also in circuit with an accumulator and a high resistance, which was varied so that the galvanometer mirror was maintained at zero deflection when no light fell on the face of the thermopile.

Calibration of Thermopile.

The thermopile, from which the funnel had been removed, was calibrated by means of a carbon filament lamp previously standardised by the National Physical Laboratory. The conditions specified for the use of the lamp in these determinations were adhered to accurately and it was found that 1 cm. deflection of the galvanometer is equivalent to a flux of 2.485×10^2 ergs per second on the circular aperture of the thermopile. It was verified by means of subsidiary calibrations with an internally electrically heated Leslie cube that the sensitivity of the galvanometer-thermopile system did not vary during the course of the research.

Corrections in the Measurement of Light Intensity.

(1) Since it is required to know the light intensity which enters and leaves the gas system, corrections must be made for reflection and absorption of light by the back faces of the reaction vessel R and the thermostat bath W. These corrections were obtained directly by finding the reduction of intensity suffered by the light beam when the reaction vessel and bath were interposed. From the measurements obtained, a comparison with the theoretical expression for light reflection made possible an evaluation of the light absorbed by each glass wall. In this way, taking the refractive index of the glass as 1.54 and using the equation

$$R = (n - 1)^2 / (n + 1)^2$$

for the fraction of light reflected, it was found that the back wall of the reaction vessel when immersed in water reflected 5.0 per cent. and absorbed 9.0 per cent. of the incident light of wave-length $365 \mu\mu$, while the back wall of the

water bath reflected 5.0 per cent. and absorbed 3.9 per cent. These corrections combine to one factor 1.27 by which the light flux on the thermopile must be multiplied to give the true flux emergent from the reacting gas system. The corresponding figures for blue light of $436\text{ }\mu\mu$ were for the back face of the reaction vessel 5 per cent. reflected and 4.7 per cent. absorbed, and for the back face of the water bath 5 per cent. reflected and 3 per cent. absorbed, which combine to the factor 1.20.

(2) It did not appear possible, except by means of a large and therefore impracticable decrease of light flux, to limit the dimensions of the incident light beam so that the whole of the light transmitted by the reaction vessel system would fall directly on the elements of the thermopile. Therefore reliance had to be placed on the efficiency of the metal funnel in reflecting on to the thermopile elements the small annular portion of the light field which fell beyond the confines of the elements. As is well known, the reflecting power of metals for light of short wave-lengths is small. It was found by observing deflections of the galvanometer when the thermopile (with and without the funnel) was at suitable positions along a converging beam of light, that the funnel reflected only 20 per cent. of the incident blue or ultra-violet light. Therefore, only 20 per cent. of the flux in the annular portion of the light beam referred to above was reflected on to the elements of the thermopile. A measure of the flux reflected by the funnel was given by the decrease in the deflection of the galvanometer resulting from the removal of the funnel, and hence the light flux falling on the funnel was given by this decrease increased in the ratio 100 : 20.

The general factor for increasing the measured value of the light flux to the true light flux was therefore obtained by evaluating the products of the appropriate factors determined under (1) and (2) above. In this way the final correcting factors 1.48 for ultra-violet ($365\text{ }\mu\mu$) light and 1.40 for the blue ($436\text{ }\mu\mu$) light were obtained.

Procedure during an Experiment.

Subject to the corrections described in the last section, the total flux of light was measured in terms of the steady galvanometer deflection produced when the shutter in front of the iris diaphragm was opened. To obtain the total absorption by the reactants, readings were made with the reaction vessel empty, both before and after the experiment. From the mean of these values was subtracted the light transmitted by the chlorine in the reaction vessel, after the nitrogen trichloride had been decomposed. Comparative experiments

showed that there was no detectable absorption by the nitrogen trichloride itself.

After the reaction vessel was filled, the chlorine very slowly attacked the rubber-free tap grease* of the various taps with which it was in communication, but after about 30 minutes, or much less for low chlorine pressures, the rate of fall of pressure due to this cause became very small and regular and could be allowed for accurately when calculating results. When the system had settled down in this way, the shutter was opened and the exposure commenced, the pressure being read at short intervals of time by following the pointer of the gauge by means of the travelling microscope. When the decomposition of the nitrogen trichloride was complete, the light transmitted by the reaction vessel and contents was determined as described above.

From the measurement of absorption of light obtained in the various experiments recorded below, Table I, the curves shown in fig. 4 were constructed,

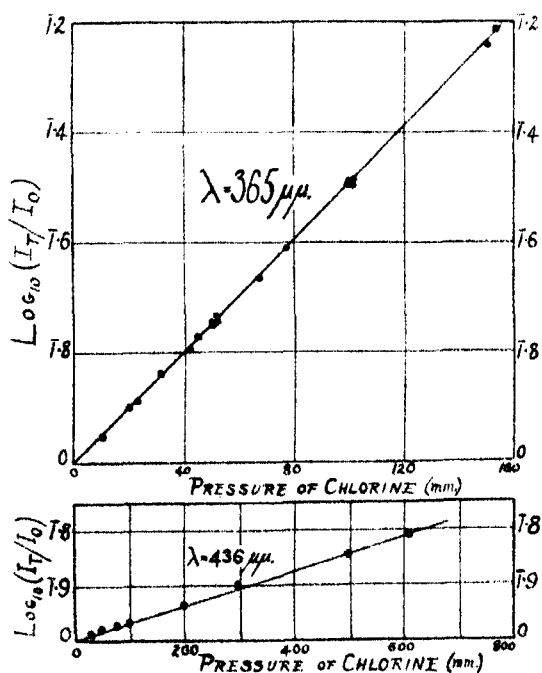


FIG. 4.

* The tap lubricant was a preparation of pure high boiling-point hydrocarbons supplied by the Shell Mex Co. under the name of Apiezon Grease "L." The very slow absorption of chlorine by this lubricant is possibly connected with the presence of some unsaturated hydrocarbon, and does not greatly affect its physical character. No irregularities were noticed in the present work as a result of its use.

in which $\log I/I_0$ is plotted against the chlorine pressure. It is seen that the straight lines for homogeneous radiation of wave-lengths 436 and 365 $\mu\mu$ pass through the corresponding experimentally determined points. From the slopes of these lines and a knowledge of the internal depth of the reaction vessel (3.5 cm.), values of the molecular extinction coefficient, ϵ , of chlorine have been calculated. In this way, it is found that $\epsilon = 27.2$ and 1.647 for $\lambda = 365$ and 436 $\mu\mu$, respectively. These results are in good agreement with those of von Halban and Siedentopf* who give the corresponding values $\epsilon = 27.17$ and 1.636.

Results.

The types of the curves showing the decomposition of nitrogen trichloride in chlorine at various pressures are shown in fig. 5. They are identical both for blue light of 436 $\mu\mu$ and ultra-violet light of 365 $\mu\mu$. After an initial rapid pressure rise the zero order of the reaction persisted practically to the end of the decomposition, the latter being signalled by a rapid kick of the gauge pointer due to some final explosive effect in the reacting mixture (Curve 1, fig. 5). The initial rapid increase of pressure was found to be identical with the Budde effect in pure chlorine at the same pressure, and is therefore attributed to the same cause. A fall of pressure of the same magnitude was observed when the shutter admitting the light to the reaction vessel was closed at the end of the decomposition.

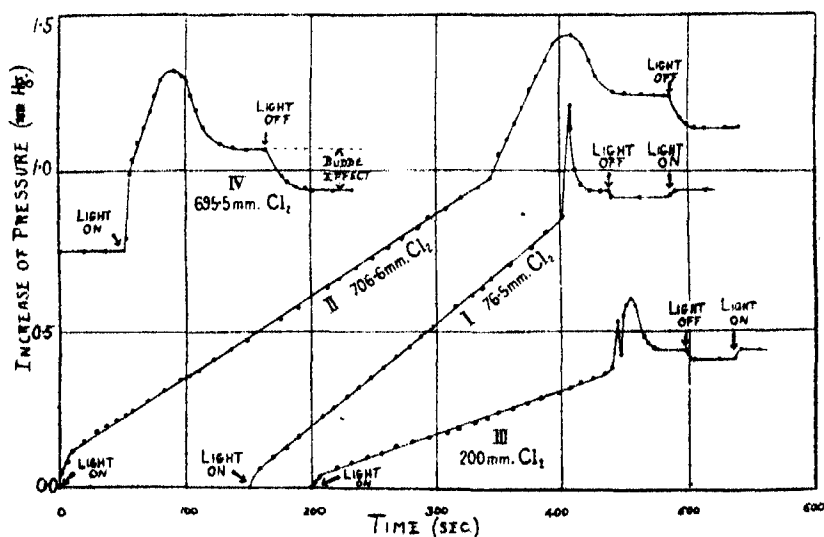


FIG. 5.

* 'Z. Physik. Chem.,' vol. 103, p. 80 (1922).

The Final Rapid Reaction.

The sharpness of the final explosion decreased greatly with increasing pressure of chlorine (see Curve II, fig. 5) an effect which suggested that its sharpness was controlled by the speed of diffusion of nitrogen trichloride molecules into the light beam. Thus if, as seems indicated, the explosion only occurs when the pressure of the nitrogen trichloride falls below some small limiting value in the light beam, the slowness of diffusion of the trichloride at high total pressures from the dark parts of the reaction vessel to the beam of light might permit of a series of incipient explosions which would be continually quenched by the intrusion of fresh nitrogen trichloride. This effect would not be observed at low total pressures, where the speed of diffusion of the nitrogen trichloride would be high enough to maintain the pressure of nitrogen trichloride in the light beam above the critical inhibiting value to a much later stage in the reaction. This view is borne out by the fact that in some cases with moderate pressures of chlorine, explosions showing two or sometimes three peaks were obtained (Curve III), suggesting a periodic reaction limited by "diffusion waves" from the dark parts of the vessel.

If, as in the case of Curve IV, the initial pressure of nitrogen trichloride was less than the limiting value for the explosive reaction this ensued immediately on irradiating the mixture, there being no slow reaction as in the case of Curve II with which Curve IV is directly comparable.

It was at first thought that this explosive termination to the reaction might be explained by the presence of small quantities of hydrogen, which upon the removal of the nitrogen trichloride detonated in the usual manner with the chlorine. This possibility was eliminated by repeated purification of the chlorine and ammonia, and by removal of all access of hydrogen to the apparatus. The magnitude of the explosive effect was entirely independent of the amounts of nitrogen trichloride used, and thus could not be due to hydrogen derived in some way from the decomposition of the ammonia.

Moreover, when all of the nitrogen trichloride in a mixture had decomposed as a result of long storage in the mixing vessel, the remaining gases did not react in any way on exposure to light. If hydrogen had been present, such irradiation would have led to an explosive reaction resulting in the production of hydrogen chloride, besides no traces of acid could be detected.

Therefore it may be concluded that the explosive termination of the photosensitised decomposition of nitrogen trichloride is a characteristic property of the reaction.

The Quantum Efficiency of the Reaction.

If P_{NCl_3} mm. of nitrogen trichloride are decomposed in T seconds, and $-d[\text{NCl}_3]/dt$ is the number of molecules decomposed per second, then, since the reaction is of strictly zero molecular order, it follows that the slope, P_{NCl_3}/T , of the pressure-time curve is given by

$$P_{\text{NCl}_3}/T = -k d[\text{NCl}_3]/dt, \quad (1)$$

where k is determined by the volume of the reaction vessel (75 c.c.) and the pressure gauge (4 c.c.) and has the value 3.88×10^{-19} . Moreover, it was found that these slopes, for any one pressure of chlorine, were directly proportional to the light absorbed over a fourfold variation of intensity, as is shown by the straight lines in fig. 6, where light flux absorbed is plotted against rate of decomposition of nitrogen chloride.

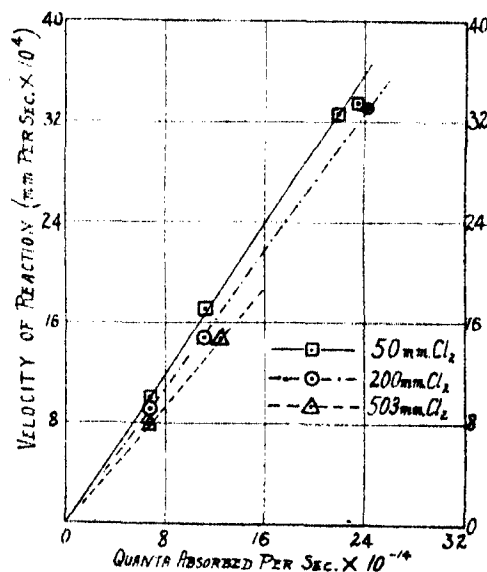


FIG. 6.

Further, if $L_{\text{abs.}}$ is the light flux absorbed, measured in quanta per second, and γ is the quantum efficiency, then

$$\gamma = \frac{-d[\text{NCl}_3]}{dt} \cdot \frac{1}{L_{\text{abs.}}}, \quad (2)$$

and hence from equation (1) above

$$\gamma = \frac{\text{slope of curve}}{k} \cdot \frac{1}{L_{\text{abs.}}}. \quad (3)$$

Photosensitised Decomposition of Nitrogen Trichloride. 605

The data are recorded in Tables I (a) and (b). In columns 3 and 4 are tabulated, in terms of observed deflection of the galvanometer, the uncorrected incident and absorbed light fluxes. $I_{abs.}$ is calculated from

Table I (a).—Homogeneous Light of Wave-length 365 $\mu\mu$.

$PNCl_2$	PCl_3	Incident light (galvano- meter deflection).	Absorbed light (galvano- meter deflection).	T.	γ obs.	γ calc.
mm.	mm.	cm.	cm.	sec.		
0.28	22.3	36.5	8.2	75	17.2	14.3
0.40	30.9	39.85	11.8	108	11.8	11.02
0.312	40.6	35.7	13.5	91	9.6	9.05
0.44	40.6	36.8	13.8	150	8.0	8.98
0.44	45.0	17.0	6.95	307	7.8	8.35
0.41	49.8	35.2	15.5	122	8.2	7.79
0.49	49.8	16.8	7.4	286	8.8	7.79
0.654	49.9	32.7	14.4	200	8.6	7.78
0.193	50.5	10.1	4.55	192	8.4	7.71
0.248	50.0	37.05	16.65	71	7.9	7.76
0.790	65.8	36.15	19.45	243	6.3	6.5
0.875	76.5	33.5	19.85	279	6.0	5.94
0.72	101.8	9.85	6.85	734	5.4	5.1
0.24	100.2	34.3	23.8	75	5.1	5.13
0.527	150.6	17.1	14.2	300	4.7	4.25
1.14	153.4	32.2	26.9	380	4.2	4.22
2.48	200.3	36.35	33.0	749	3.8	3.82
0.40	203.7	10.1	9.2	438	3.8	3.8
0.434	200.0	16.8	15.2	290	3.7	3.82
0.60	298.7	35.75	34.65	175	3.7	3.38
0.785	395.4	19.05	19.0	501	3.1	3.16
0.56	397.1	35.1	34.55	188	3.3	3.16
1.06	503.7	10.1	10.1	1334	3.0	3.02
0.425	505.6	18.7	18.7	288	3.0	3.02
0.624	549.6	35.6	35.5	208	3.2	2.98
0.860	669.9	36.1	36.1	312	2.9	2.89
1.14	706.6	31.6	31.6	454	3.0	2.87

Table I (b).—Homogeneous Light of Wave-length 436 $\mu\mu$.

$PNCl_2$	PCl_3	Incident light (galvano- meter deflection).	Absorbed light (galvano- meter deflection).	T.	γ obs.	γ calc.
mm.	mm.	cm.	cm.	sec.		
0.166	32.9	26.15	0.60	675	13.7	10.5
0.302	50.1	24.75	0.87	1575	7.4	7.75
0.340	76.9	24.35	1.23	1670	5.6	5.92
0.286	101.4	25.4	1.70	1225	4.6	5.1
0.320	202.3	19.45	2.64	1050	3.9	3.8
0.383	299.3	26.05	4.9	825	3.2	3.38
0.355	500.5	22.6	6.8	585	3.0	3.03
0.146	608.5	25.4	8.9	190	2.9	2.93

these with the aid of the light flux corrections and galvanometer calibration described above. $\gamma_{\text{obs.}}$ is evaluated by means of equation (3).

It was also found that the quantum efficiency was inversely proportional to the pressure of chlorine, as is shown by the straight line obtained when γ is plotted against $1/P_{\text{Cl}_2}$ (fig. 7).

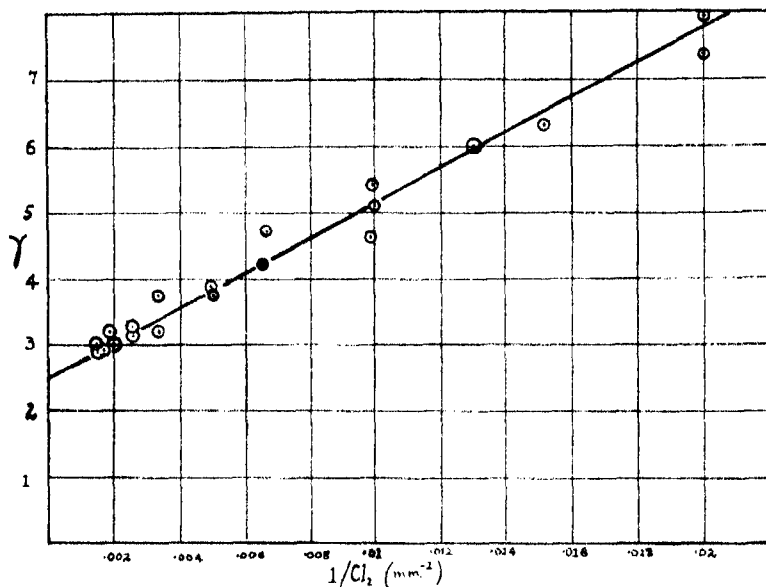


FIG. 7.

The quantum efficiency, γ , is therefore given by the equation

$$\gamma = k_0/P_{\text{Cl}_2} + k_1, \quad (4)$$

where k_0 is determined by the slope of the line in fig. 7 and k_1 is the intercept of the line on the axis of γ . In this way it was found that $k_0 = 263$ or $1/0.0038$ and $k_1 = 2.5$ both for blue and ultra-violet light, so that equation (4) becomes

$$\gamma = \frac{1}{0.0038 P_{\text{Cl}_2}} + 2.5,$$

and is valid for light wave-lengths of 436 and 365 $\mu\mu$. The values of $\gamma_{\text{calc.}}$ in Table I are calculated from this equation which is plotted accurately in fig. 8, and the degree to which the experimental determinations conform to it may be gathered from the distribution of points along the curve. The quantum efficiency thus varies from high values at low chlorine pressure, to a limiting value in the neighbourhood of 2 when the pressure is increased, and in addition

to its positive photosensitive action we must therefore ascribe to the chlorine an inhibiting effect proportional to its pressure.

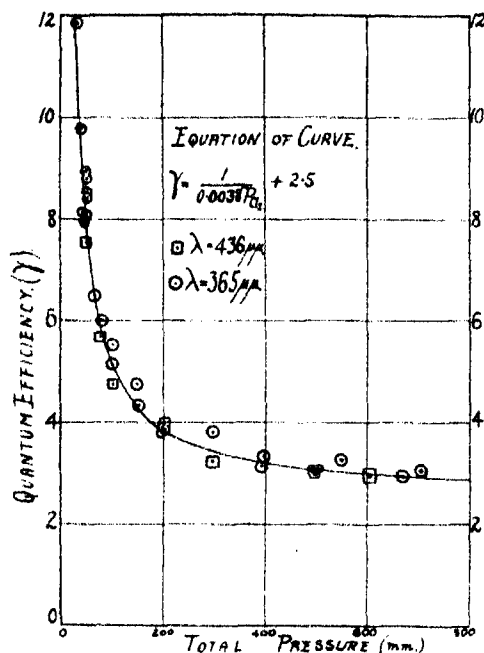


FIG. 8.

Conclusions.

The foregoing experimental results establish the following facts:—

(1) When chlorine containing small quantities (up to 3 mm.) of nitrogen trichloride is illuminated by light of wave-length 436 or 365 $\mu\mu$, the latter substance is decomposed in a strictly zero order reaction by the photosensitive action of the chlorine.

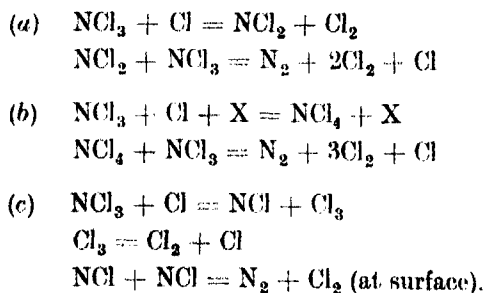
(2) The quantum efficiency is the same for blue light of $\lambda = 436 \mu\mu$ as for ultra-violet light of $\lambda = 365 \mu\mu$. It reaches high values (up to $\gamma = 20$) for low pressures of chlorine and falls hyperbolically to a limiting value of $\gamma = 2.5$ as the pressure of chlorine is increased. A chain reaction of some sort therefore appears to be indicated, the length of chain being shorter the greater the pressure of chlorine.

(3) The reaction is terminated by a sudden pressure leap which would appear to be due to an explosive evolution of heat when the pressure of the nitrogen trichloride falls below a certain limiting value; this kick is the more marked the lower the chlorine pressure, and the facts are consistent with the view that

the sharpness is controlled by the rate of diffusion of the last traces of the nitrogen trichloride into the light beam.

The order of the reaction would at first suggest a surface decomposition, as has already been assumed by one of us in the earlier experiments on the mechanism of the induction period referred to above (Norrish, *loc. cit.*). Against this, however, we have the high quantum efficiencies at low pressure, which would introduce the difficulty (not necessarily insurmountable) of associating a chain or clustering mechanism with the surface reaction. The explosive termination of the reaction, however, which certainly has its seat in the body of the gas adds a more serious difficulty, and would seem to drive us back to consider the possibility of the whole decomposition being a homogeneous gas reaction.

Granted that the first action of the light is to dissociate the chlorine molecule into atoms, we may ask ourselves—what would be the fate of these atoms in an atmosphere of nitrogen trichloride? Since it is generally agreed that their rate of recombination is slow we may suppose that they will persist long enough to meet molecules of nitrogen trichloride during the lifetime of the order of 0.01–0.1 second. The following chain reactions may be suggested :—



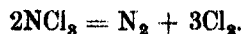
The explosive termination might be associated with the building up of one or other of the intermediate compounds postulated above.

The present facts in spite of the great simplicity of the relationship found are insufficient to distinguish finally between the possibilities of a surface or homogeneous decomposition, nor is it at present profitable to speculate further upon the chain mechanism suggested above. Further important evidence becomes available by a study of the effect of varying the dark and the illuminated surface, and the effects of foreign gases, the results of which will be described in Part II of this series.

Summary.

1. The induction period produced by ammonia in the photochemical combination of hydrogen and chlorine is due to nitrogen trichloride formed by interaction of chlorine and the ammonia.

2. The decomposition of nitrogen trichloride in chlorine alone is photo-sensitised by chlorine and the net reaction is given by the equation



3. The reaction is of strictly zero molecular order with respect to the nitrogen chloride until the decomposition is almost complete; then a semi-explosive reaction occurs.

4. The velocity of the zero order reaction is directly proportional to the light flux absorbed by the chlorine.

5. The quantum efficiency (γ) of the zero order reaction in homogeneous blue ($436\text{ }\mu\mu$) and ultra-violet ($365\text{ }\mu\mu$) is high (< 20) at low pressures of chlorine and decreases with increase of chlorine pressure, P_{Cl_2} , to a limiting value in the neighbourhood of 2. The results are reproduced by the equation $\gamma = 1/0.0038 P_{\text{Cl}_2} + 2.5$.

6. No decomposition occurs in yellow ($579\text{ }\mu\mu$) or green ($546\text{ }\mu\mu$) light.

7. The reaction is probably initiated by chlorine atoms and proceeds by way of reaction chains of short length.

Acknowledgments.

The authors wish to express their thanks to the Government Grant Committee of the Royal Society and the Research Grant Committee of the Chemical Society for grants towards the purchase of apparatus, and to the Governing body of Emmanuel College for a research grant to one of us (J.G.A.G.).

*The Discontinuous Nature of the Process of Sorption of Gases
and Vapours by Porous Solids.*

By A. J. ALLMAND, F.R.S., and L. J. BURRAGE, King's College, London.

(Received January 13, 1931.)

During the last five years, a mass of evidence has accumulated in this laboratory pointing to the conclusion that the adsorption of vapours by charcoal is an essentially discontinuous process, and that, for example, an ordinary adsorption isothermal is composed of a series of loops, cutting one another at more or less well-defined pressures. We were for long inclined to attribute such discontinuities to casual experimental error, or to defects inherent in the technique used. As, however, improvements in the latter have so far not led to the elimination of these "breaks," but rather to their more certain definition, and as similar results are beginning to appear from other laboratories, we think it well to present an account of our conclusions, and of the evidence on which they are based.

1. *Adsorption of Vapours by Charcoal at Low Pressures (Pirani Gauge Measurements).*

The first indication of the existence of discontinuities was obtained in these experiments, of which the technique has been described by Chaplin.* A definite break was found on the 25° C. carbon tetrachloride isothermal of charcoal F† at 0.096 mm.,‡ and breaks were discovered in all isosteres,§ whatever the charcoal used, at about the same pressure. Later work|| showed breaks to exist in the 25° C. carbon tetrachloride isothermal of charcoal B¶ at about 0.1 mm. and at adjacent somewhat higher pressures. More recently, further (unpublished) isostere measurements have been made by Dr. E. G. V. Barrett, using carbon tetrachloride, and by Mr. J. L. Lizius, using carbon bisulphide, in both cases with several charcoals. A break has invariably been found at 0.1 mm. or at a slightly higher pressure. In addition, determinations

* 'Proc. Roy. Soc.,' A, vol. 121, p. 344 (1928).

† *Loc. cit.*, p. 356. A steam activated coconut charcoal.

‡ Allmand and Chaplin, 'Proc. Roy. Soc.,' A, vol. 129, p. 246 (1930).

§ *Loc. cit.*, p. 257.

|| Allmand and Puttick, 'Proc. Roy. Soc.,' A, vol. 130, p. 197 (1930).

¶ 'J. Phys. Chem.,' vol. 32, p. 452 (1928). A pinewood charcoal activated by zinc chloride.

of the adsorption isothermals of mixtures of carbon bisulphide and of water vapour also give evidence of these breaks (unpublished work of Mr. Lizius).

2. *Adsorption of Vapours by Charcoal in presence of Air (Retentivity Technique).*

A simple so-called "retentivity" method for the *approximate* determination of the adsorption isothermals of vapours on charcoals was worked out some time back by Allmand, Manning and Burrage.* It yields curves each of which consists of a series of loops. The results of such a test carried out at 25° with water vapour and charcoal B, from which much of the mineral content had been removed by desublimation *in vacuo* at 300° C., are shown in fig. 1, on

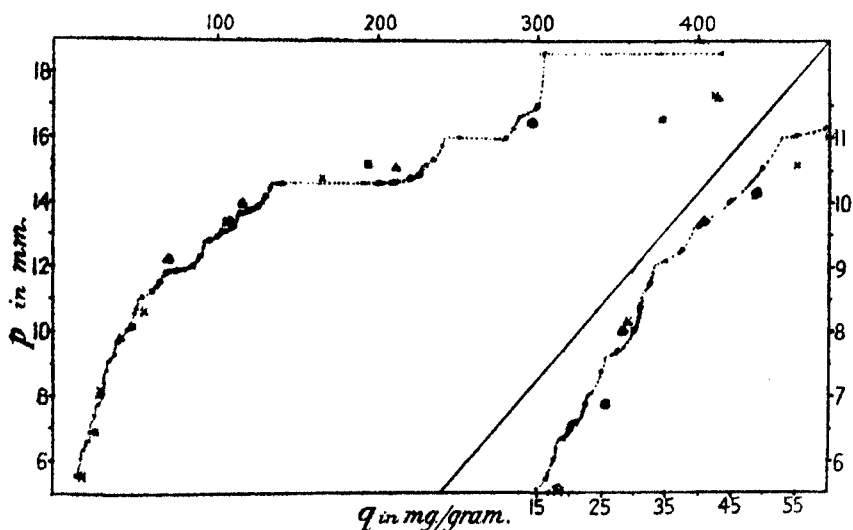


FIG. 1.

which are also indicated the experimental points found on the *adsorption* branches of various isothermals during work done some years earlier with water vapour and the same charcoal. The crosses refer to measurements on sorption from a moist stream of air,† and the triangles and squares to two series of data obtained by a static technique, working in absence of air.‡ The horizontal portions of the "retentivity" isothermal correspond, of course, to those portions of the retentivity curve of constant slope.

* 'J. Soc. Chem. Ind.,' vol. 47, pp. 369r, 372r (1928).

† Allmand, Chaplin and Shiels, 'J. Phys. Chem.,' vol. 33, p. 1151 (1929), fig. 3.

‡ Allmand, Hand, Manning and Shiels, 'J. Phys. Chem.,' vol. 33, p. 1682 (1929), fig. 2.

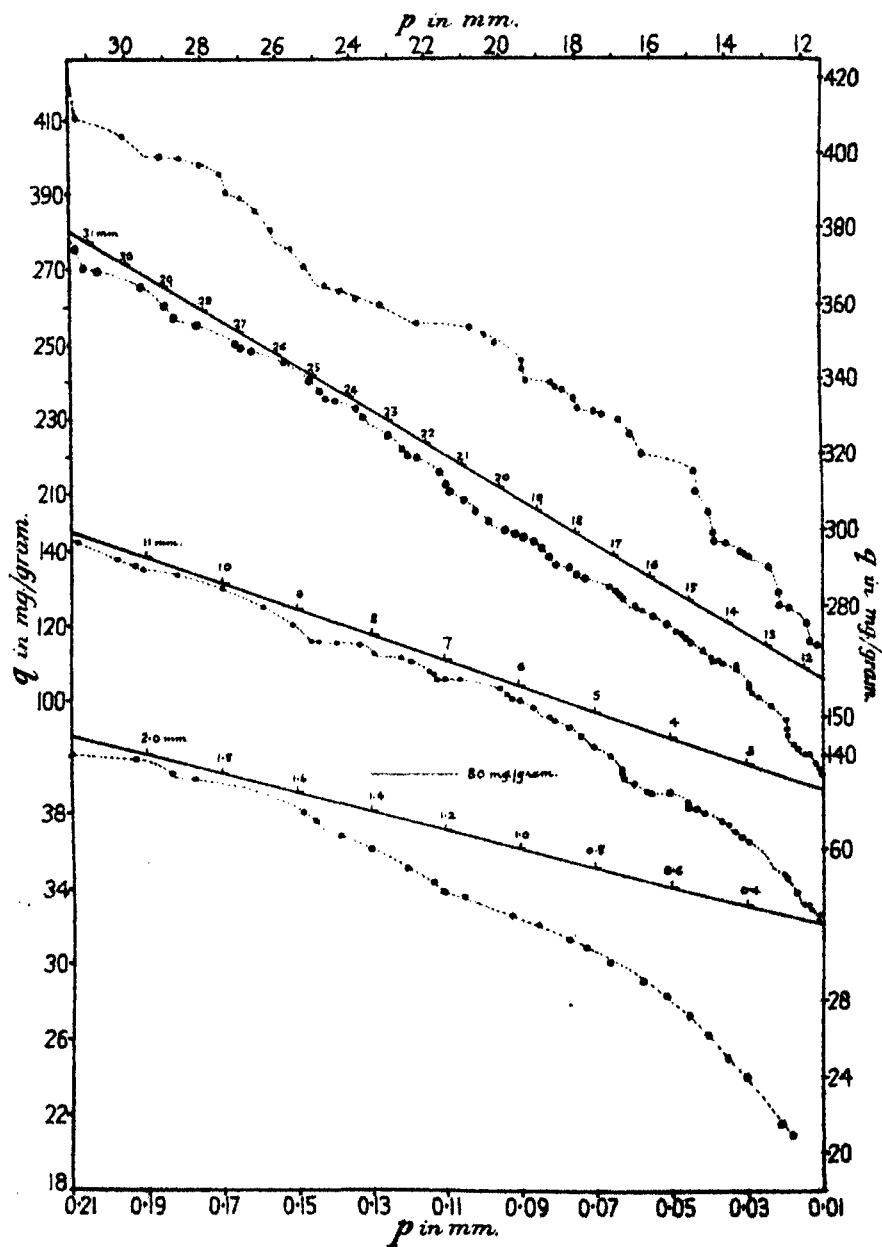


FIG. 2.

The "simple retentivity test" was later developed by Burrage into a method giving *true* adsorption isothermals,* and many such determinations

* 'J. Phys. Chem.,' vol. 34, p. 2202 (1930).

have been carried out, both with carbon tetrachloride (from 33 mm. pressure downwards, at 100° and at 25°) and with water vapour (from a maximum of 18 mm. pressure downwards, at 25°). In every case, these isothermals have proved to be discontinuous, showing a large number of breaks, of which the lowest, in all the most reliable experiments, was in the neighbourhood of 0·1 mm. pressure, whether the sorbate was water vapour or carbon tetrachloride, and whether the temperature was 100° or 25°. Attempts to discover any definite regularities in the pressure values characterising the breaks at higher pressures, or in the quantities of sorbate taken up between two successive discontinuities in the isothermals, have hitherto been unsuccessful, although indications of such concordance in the case of the pressure readings have certainly been observed. Further details of these experiments are being published elsewhere, and fig. 2 merely contains a favourable example of the type of result obtained (carbon tetrachloride isothermal for charcoal G* at 100° C.).

3. Adsorption of Vapours by Charcoal at Moderate Pressures in absence of Air.

The results just described, unforeseen in their nature and depending on a new technique, clearly called for confirmation. For this purpose, experiments were carried out by a static method, using thoroughly degassed charcoals, working in absence of air, and measuring the equilibrium pressures by a mercury manometer. The first results of this kind have already been described.† They were obtained at 25° C. with carbon tetrachloride and charcoal B, over pressure ranges, in two experiments, covering 0·28 to 70·45, and 17·94 to 31·74 mm. respectively. They confirmed beyond question the discontinuous nature of the isothermal, but the measurements were not sufficiently numerous to define its structure in detail.

During 1928–29, we did a number of similar measurements, with the primary object of extending the work to other sorbates. The experiments, with one exception, were carried out at 25°, and included the determination of the following isothermals (see Table I).

The static apparatus and method employed were simple and apparently effective. The charcoal container, in a thermostat at 25° (at 40° during experiment (viii)), could be connected by taps with (a) a Leyboldt mercury diffusion pump, backed by a Hyvac pump, and with a McLeod gauge for esti-

* 'J. Soc. Chem. Ind.,' vol. 47, p. 372r (1928). A steam activated palm nut shell charcoal.

† Allmand and Puttick, *loc. cit.*

Table I.

Experiment.	Charcoal.	Sorbate.	Pressure range in mm.	Number of experimental points.	Number of points per millimetre of pressure range.
(i)	L*	CS ₂	19.2-0.6	60	3
(ii)	L	CCl ₄	9.5-5.9	33	9
(iii)	B	C ₂ H ₆	8.8-6.2	15	6
(iv)	B	H ₂ O	9.6-6.3	18	5
(v)	B	n-C ₈ H ₁₇ OH	3.0-0.13	52	17
(vi)	J†	C ₂ H ₆	5.1-0.8	50	12
(vii)	D1‡	CO ₂	4.6-2.6	12	6
(viii)	D1	CO ₂	8.0-5.3	12	4

* 'J. Phys. Chem.,' vol. 34, p. 2202 (1930). A steam activated soft-wood charcoal.

† 'J. Phys. Chem.,' vol. 33, p. 1682 (1929). A sugar charcoal.

‡ A steam activated nut shell charcoal of British origin. Bulk density of 10-12 mesh granules, 0.575.

mating the efficiency of the evacuation; (b) a mercury manometer reading to 0.01 mm. by a cathetometer; (c) a bulb containing a supply of the liquid sorbate previously purified by successive refractionations; (d) a tube immersed in a refrigerant for holding down the vapour under investigation whilst pumping off gases displaced from the charcoal.

The charcoal was first air-dried at 150° and then, after filling into the container, evacuated cold down to 1×10^{-4} mm., and then finally at 110° to the same pressure before weighing. It was initially charged up to a pressure about double that at which the first point was required, and left overnight at 25° in order to displace the great bulk of carbon dioxide from the charcoal.* The largest quantity of this gas was given by charcoal L when working with carbon bisulphide. After weighing the container and re-attaching the apparatus, the latter was pumped down to about 10^{-4} mm., closed off from the pumps, and the container tap opened so as to admit vapour to the manometer system. When equilibrium had been established, which happened very quickly, the container tap was shut, the manometer read off, the vapour charge in the apparatus freed from any displaced gas by means of the freezing tube and suitable refrigerants in the usual manner,† and the pressure of the residual pure vapour determined. The accuracy with which this could be done was considerable. Successive resettings of the cathetometer usually gave the same

* Allmand and Chaplin, *loc. cit.*, p. 262.

† Chaplin, *loc. cit.*, p. 354.

result to 0.01 mm., and this figure must be regarded as the maximum normal error in making the actual readings.

Knowing the volume of the apparatus (355 c.c.), the amount of vapour withdrawn from the container and hence the amount still remaining in it were calculated, the data for a point on the isothermal thus being obtained. Subsequent desorption points were determined in a similar manner, by opening up the apparatus for an instant to the pump and thus withdrawing a small amount of vapour, measuring the pressure, putting the container into connection with the apparatus and, after a new equilibrium pressure had been set up, proceeding as described above. At the close of the experiment, the container was detached and reweighed, thus giving a check on the accuracy of the previous measurements and deductions, which had been made assuming the validity of the ordinary gas laws. Reasonably close agreement between the found and calculated final values of q was obtained. When determining sorption points, the procedure was similar, except that, after the final reading off of each pressure, the apparatus was connected with the supply of sorbate, instead of with the pump circuit.

The above technique allows of rapid working, and points can readily be obtained close to one another on the isothermal. Nevertheless, in some cases (experiments (i), (iii) and (iv)), the amounts of sorbed vapour were determined by direct weighing after each pressure measurement, and not as just described. This, of course, meant a considerably slower rate of work.

The details of the different experiments were as follows :—

Experiment (i). Charcoal L and Carbon Bisulphide.—This consisted of one long series of desorption points. The results are plotted logarithmically in fig. 3 which also contains, inset, two sections of the data plotted in the form of p against q . The discontinuities shown far exceed the experimental error in a number of cases. It is clear that, above point 6 and below point 57, the number of readings is insufficient to define the course of the curve. Very considerable carbon dioxide pressures were found in the vapour phases in equilibrium with the charcoal early in the experiment. Thus, the values at the first six experimental points were respectively 9.84, 3.54, 0.10, 0.20, 0.26 and 0.21 mm. of mercury. After point 12 (9.28 mm. of carbon bisulphide; 364.4 mg. per gram) the apparatus was allowed to stand for 7 days before point 13 was taken. This resulted in the carbon dioxide pressure rising to 0.50 mm. Subsequently it fell off, sometimes rather spasmodically (the pressures observed at points 16 to 18 were respectively 0.10, 0.40 and 0.02 mm.)

and was undetectable (i.e., below 0.01 mm.) from point 30 to the end of the experiment.

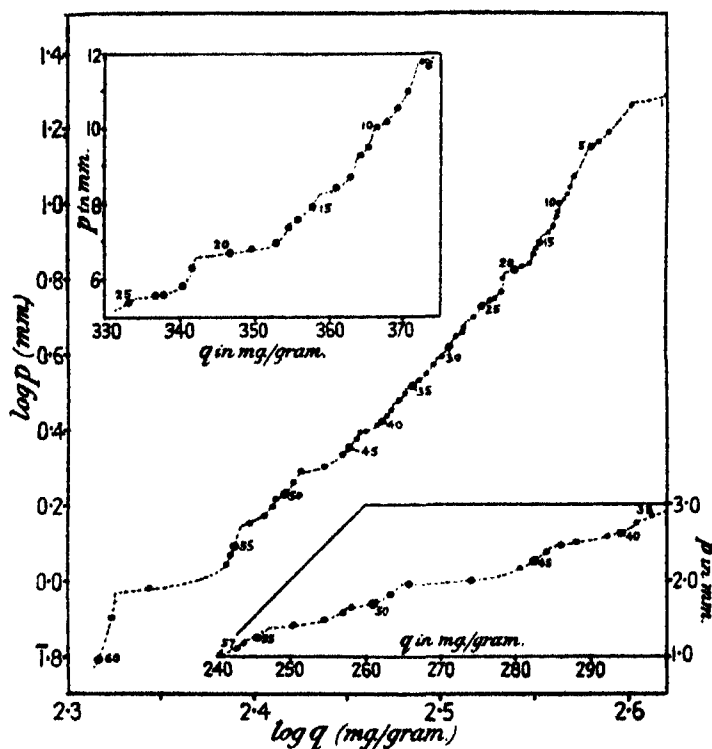


FIG. 3.

These carbon dioxide pressures were far greater than those observed in other cases. Whether carbon bisulphide has any particular displacing action on the surface gases is doubtful. Quite possibly the large effect was merely due to the high charging pressure used in the experiment.

Experiment (ii). Charcoal L and Carbon Tetrachloride.—Special attention was paid in this case to the question of reversibility,* and four successive series of points were taken, the first (16 points—full circles) and the third (6 points—circles) being desorption, and the second (8 points—squares) and the fourth (3 points—triangles) resorption measurements. As is seen in fig. 4 they all lie satisfactorily on a single broken curve.

* The results mentioned at the beginning of this section as obtained with charcoal B and carbon tetrachloride already gave some indication of the reversible nature of these discontinuous isothermals. See Allmand and Puttick, *loc. cit.*,

The q value checked at the end of the experiment gave 536.0 mg. per gram, the computed figure being 537.27 mg. per gram. No carbon dioxide was

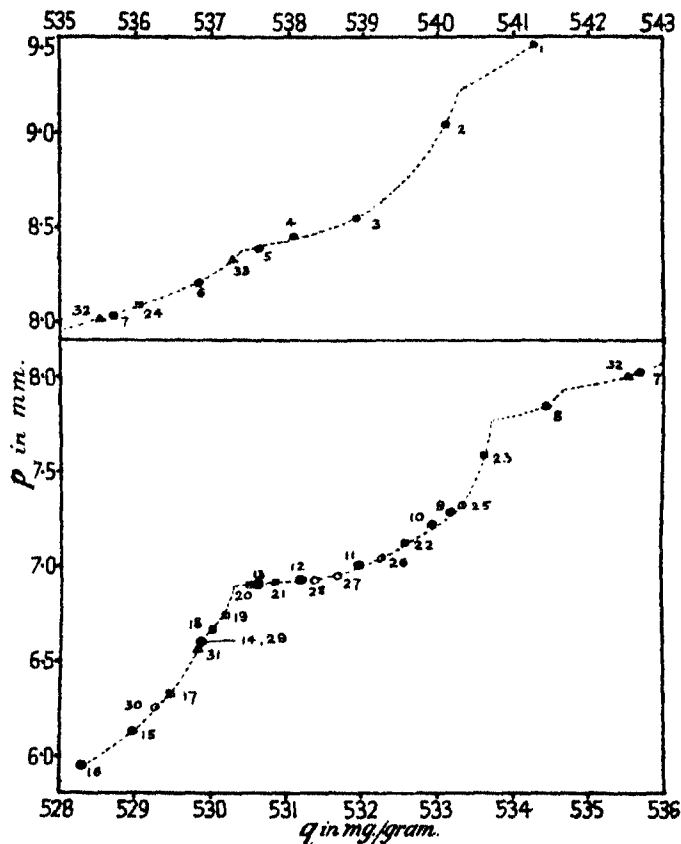


FIG. 4.

noticed except during the last two resorption points, when pressures of 0.34 and 0.52 mm. respectively were developed.

Experiment (iii). Charcoal B and Benzene.—In this case, two desorption points and a resorption point were succeeded by 12 further desorption points. The results are shown in fig. 5, Curve I. At no stage did the carbon dioxide pressure exceed 0.01 mm.

Experiment (iv). Charcoal B and Water.—See fig. 5, Curve II. Seventeen desorption points, commencing with 9.64 mm., were first determined. These were succeeded by two resorption and three further desorption points. The four last points are plotted separately in inset (a). It will be seen that the q values are considerably greater than in the first desorption series. This

"drift" towards increased sorption (at any particular pressure) as the maximum charging pressure to which the charcoal has been subjected increases, is very

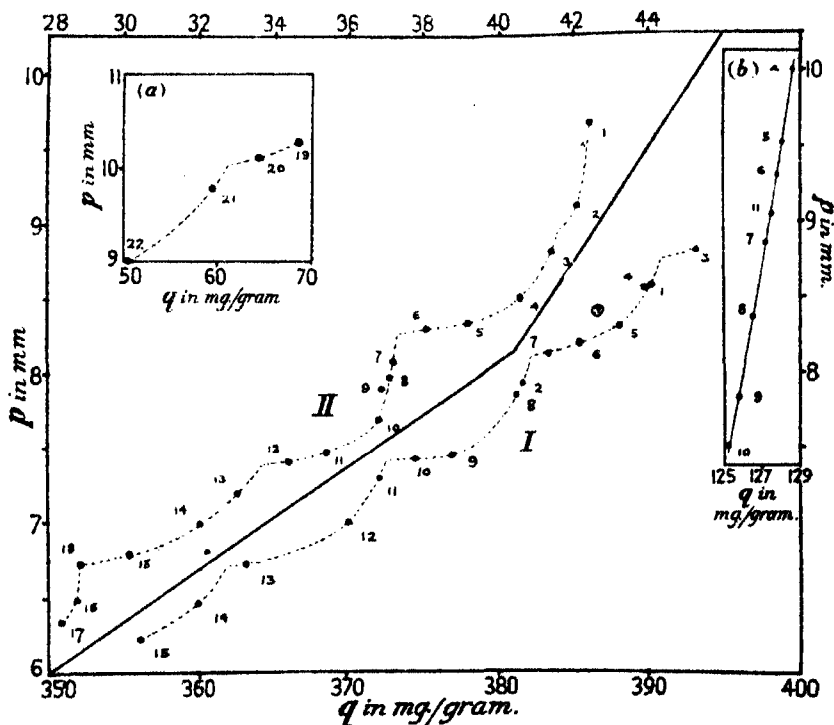


FIG. 5.

marked with water vapour,* and we now have reason to think that the slowness of the displacement of carbon dioxide from the charcoal surface is the cause, water vapour being relatively ineffective in this respect.†

In the present case, the carbon dioxide pressure actually read off when measuring point 1 was 0.22 mm. This decreased to 0.06 mm. at point 5, after which no more was detected until the high charging pressure of point 19 was reached, when the figure was 0.16 mm., followed by 0.10 mm. at point 20. These figures may well be lower than the actual pressures, owing to solubility of carbon dioxide in ice. On the other hand, charcoal B has given evidence in other experiments of evolving comparatively little carbon dioxide when treated with vapours.

Experiment (v). Charcoal B and *n*-Amyl Alcohol, which was chosen as being

* Allmand, Hand and Manning, 'J. Phys. Chem.,' vol. 33, p. 1694 (1929).

† Allmand and King, 'Proc. Roy. Soc., A, vol. 130, p. 216 (1930).

a hydroxylic liquid of considerably lower vapour pressure than water. It was anticipated that any breaks obtained would be very well marked, even more pronounced than those shown in fig. 1. As will be seen, however (fig. 6),

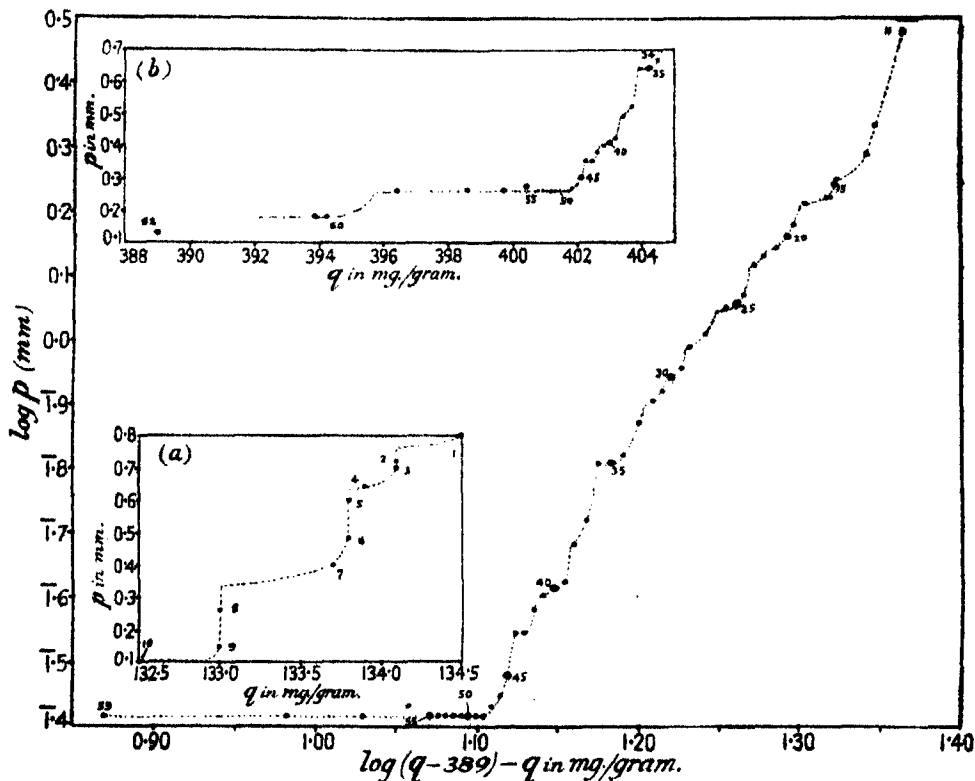


FIG. 6.

the isothermal, over the pressure range covered, gave a number of small but well-defined breaks, with indications of the existence of large loops at still lower pressures.

Prior to the main desorption experiment referred to in Table I, a series of 10 desorption points covering the range of 0.8 to 0.1 mm. was measured, the q values being determined by direct weighing. The results are shown in inset (a). In three cases, when passing between successive points, a marked drop in pressure was observed without any measurable change in q . No detectable carbon dioxide pressures were developed, and there was no observable tendency to drift when the apparatus was allowed to stand for 18 hours after measuring point 2.

When, however, the container was recharged to a higher pressure for the

main series of measurements, starting with point 11 at 3.00 mm. pressure, it was found that the quantity of sorbate taken up by the charcoal had enormously increased. During the desorption series which followed (51 further points), whilst the pressure fell to 0.13 mm., the q values only dropped from 412.1 to 389.0 mg. per gram. The pressure range of 0.80 to 0.26 mm., which corresponded in the first series to a q range of 134.5 to 133.0 mg. per gram now corresponded to 405 to 396 mg. per gram. It is clear that the effect of initial charging pressure in producing drift is as great as, or greater than, is the case with water. A carbon dioxide pressure of 0.03 mm. was observed when determining point 11, but none was noticed subsequently. Moreover, after point 14, the apparatus was allowed to stand for 48 hours. There was no perceptible drift.

The estimated q values were checked by direct weighing after points 35 and 56. The found values (estimated figures in brackets) were respectively 404.6 (404.27) and 400.2 (400.43) mg. per gram. It should be added that, although the amyl alcohol had been carefully refractionated and was apparently a very satisfactory specimen, the mercury of the manometer was nevertheless somewhat attacked, and more difficulty than usual was encountered in getting satisfactory readings.

As the chief purpose of these experiments is merely to demonstrate the complex structure of the isothermals, the bulk of the data in the present case (points 11 to 59) have been plotted in the convenient form of $\log p$ against $\log (q-389)$, where q , as always, denotes milligram per gram. There are seen to be numerous breaks, some of them very well marked, particularly that at 0.26 mm. (points 48 to 59). Inset (b) contains points 34 to 62 plotted in the form of p against q .

Experiment (vi). Charcoal J and Benzene.—This experiment was undertaken to see whether the fine structure shown by the isothermals so far described was in any way connected with the retention by the charcoals of the morphological structure of the raw materials used in their manufacture. Microscopic examination showed charcoal B to possess such a structure to a high degree. Charcoal L is a briquetted material, but vestiges of the structure of the original beechwood would certainly be expected to persist. The isothermals given by the sugar charcoal J would be free from any such effect.

The 50 points obtained, all belonging to the same desorption series, are plotted in fig. 7. Whilst the majority of the breaks are slight, some being on the limit of the experimental error, a few are very well marked. No carbon dioxide evolution was detectable at any point during the experiment, and

18-hour tests for drift, made after points 6, 10 and 49, yielded negative results. The q value found by direct weighing after point 50 was 238 mg. per gram, as against an estimated figure of 241.45 mg. per gram.

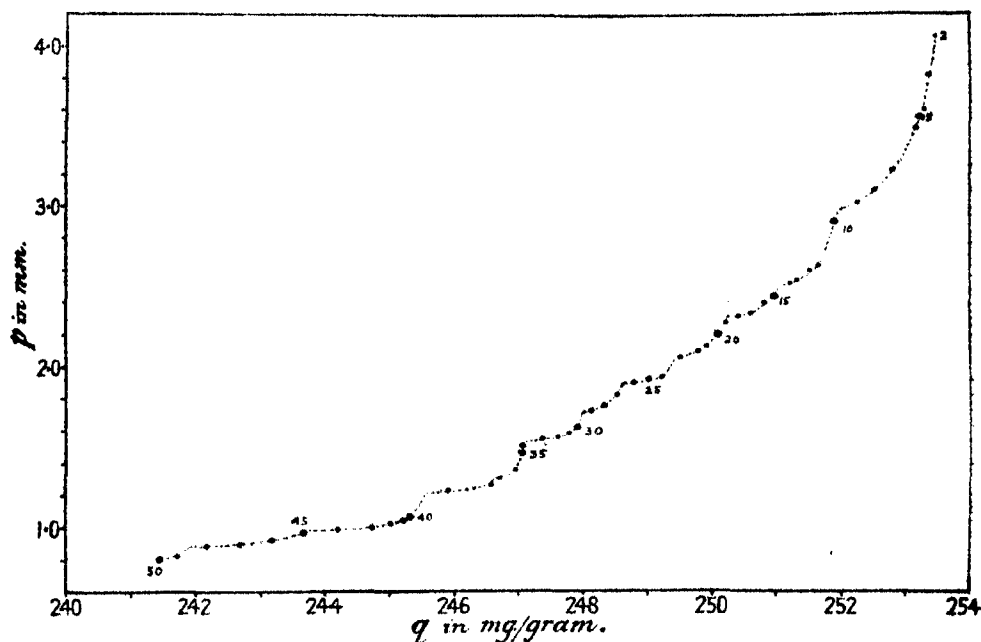


FIG. 7.

Experiment (vii). Charcoal D1 and carbon dioxide, chosen as being a gas and not an easily condensable vapour. Twelve desorption points were taken, the q values being determined by direct weighing in points 1 to 3. Omitting the first reading (4.58 mm., 4.53 mg. per gram) as being rather far removed from the remaining points, the results are plotted in fig. 8, curve I. There are definite indications of breaks, although, as anticipated, these are not very well marked. A test for drift after point 9 gave no result in 18 hours. After point 12, a check weighing of the container gave $q = 3.3$ mg. per gram, whereas the estimated figure was 3.306 mg. per gram.

Experiment (viii). Charcoal D1 and Carbon Dioxide.—Having obtained the above result below the critical temperature of the sorbate, it was of interest to see whether the same type of behaviour was shown above the critical temperature. Accordingly, a similar experiment to (vii) was carried out at 40° C. After three preliminary readings at pressures of about 2 mm., the charcoal was charged up to a higher pressure, and point 4 taken at 8.04 mm.

and 7.54 mg. per gram. Ten further desorption points were measured, and a final resorption point (No. 15). An 18-hour drift test with negative results

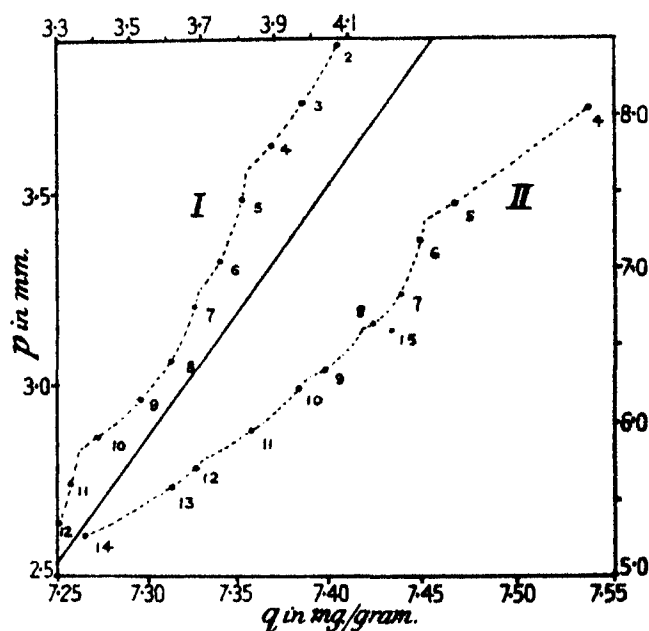


FIG. 8.

was carried out after point 10. Direct weighing after point 15 showed q to be 7.3 mg. per gram, the estimated figure being 7.43 mg. per gram. The results for points 4 to 15 are plotted in fig. 8, curve II, and again show the presence of breaks, one of these being well marked.

There are, however, certain comments to be made on these last two experiments. No test for "displaced carbon dioxide" could naturally be carried out, and the absence of drift on standing was anticipated, in the light of the similar results obtained with water and amyl alcohol vapours. Nevertheless, it is clear that the isothermals are far from representing equilibrium. The resorption point 15 in experiment (viii) shows clear indication of drift. Moreover, a comparison between the unplotted point 1 of experiment (vii) and the lowest pressure points of experiment (viii) would suggest that less carbon dioxide is taken up at 25° than at 40°. So also would the results of the three preliminary unplotted points of experiment (viii), which were as follows:—

Point	1	2	3
Pressure in mm.....	2.14	2.11	2.08
q in mg./gram	3.94	3.91	3.89

The "equilibrium" pressures found at 25° with similar charges of carbon dioxide were about 3.7 mm., thus far higher than at 40°. It may be added that Dr. R. Chaplin (unpublished work) has shown that charcoals of the type of D1 exhibit very considerable drift when sorbing carbon dioxide at pressures of the order of 10^{-1} to 10^{-2} mm.

An obvious criticism is that the discontinuities observed in these last experiments may depend on the fact that true equilibria were not being measured. Work now in progress appears to indicate that this is not the case.

4. Adsorption of Vapours by Silica Gel.

In order to be able to compare our results with the precise experiments of Lambert and Clark,* an experiment was carried out with benzene, using the technique described in the last section. A specimen of commercial silica gel was employed, previously evacuated at 110° C. to "constant weight."

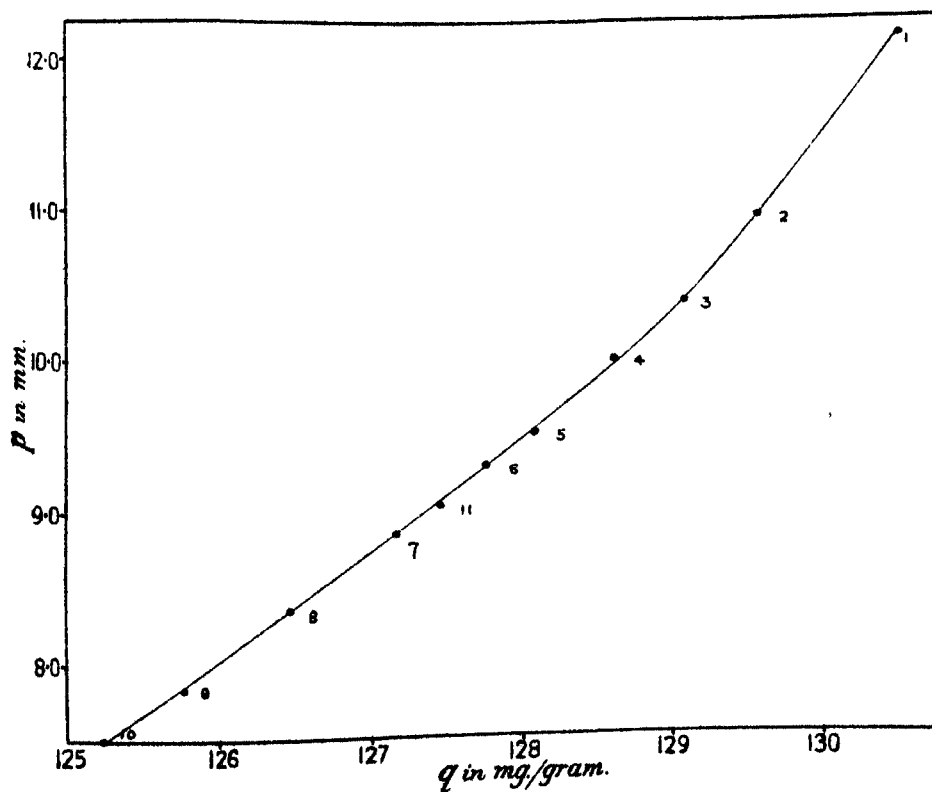


FIG. 9.

* 'Proc. Roy. Soc.,' A, vol. 122, p. 497 (1929).

A desorption series of 10 points was determined and then a final resorption point. The results are plotted in fig. 9; point 11 is seen to fall very near indeed to the main curve. It is obvious that any "breaks" which exist are relatively slight, and this fact is emphasised in fig. 5, where the isothermal (inset (b)) is drawn on the same p and q scale as the isothermal for benzene on charcoal B (curve I).

As nevertheless it was just possible that slight discontinuities of the order of the experimental error were present, it was decided to do experiments by the simple retentivity technique (a single 28 mm. column), employing the same gel as sorbent, and using water and carbon tetrachloride as sorbates. The approximate 25° C. isothermals which resulted are shown in fig. 10. The lower curve,

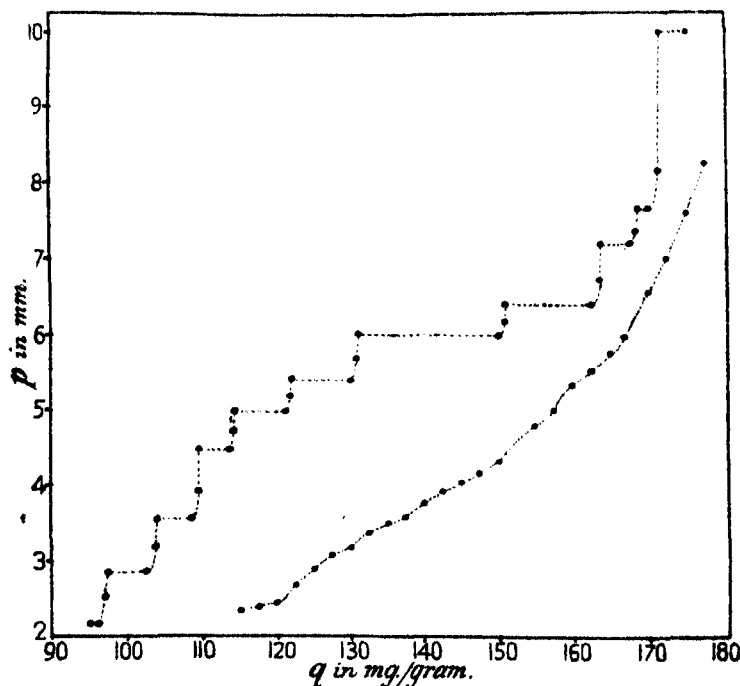


FIG. 10.

for carbon tetrachloride, exhibits points of inflection and irregularities which definitely indicate the existence of slight breaks. A comparison between its course above 6 mm. pressure and the curve in fig. 9 suggests that, if the static experiment with benzene had been continued down to lower pressures, definite evidence of breaks would have been found.

The upper curve, for water vapour, is a remarkable one. The corresponding

retentivity curve consisted essentially of a series of straight lines of decreasing slope, tending to cut one another sharply, the change in slope being completed over a very small q range. The result is the "stepped" type of isothermal shown, in which the sudden p and q changes are certainly not exaggerated. This is the most extreme example of discontinuous isothermal structure we have so far encountered.

5. *Experiments of other Observers.*

The reason why the existence of these breaks has, in general, escaped the notice of others is, we think, a simple one, viz., that, even in the best work, the experimental points have been spaced too widely apart. Inspection of Table I and of the diagrams will show that in no case in the present instance (when working with charcoal) have we determined an average of less than three experimental points per millimetre of pressure range, and that, in one case (experiment (v)), this number rose to about 17. These numbers have by no means always sufficed to define with accuracy the detail of the isothermal concerned; in fact, in some instances, even the *number* of breaks in a given pressure range is uncertain. In the work of Allmand and Puttick,* an average of three experimental points per 2 mm. pressure proved insufficient to determine with accuracy the course of the isothermal. The density of points necessary for this purpose will, of course, vary from case to case, depending on the sorption pressure, the vapour pressure and nature of the sorbate, and the nature of the sorbent.

When we turn to other published work, we find no such profusion of experimental points. Thus, Goldmann and Polanyi,† working with carbon bisulphide on charcoal at 20.5° C., have eight points covering the range of 8.9×10^{-2} to 57 mm.; Lambert and Clark,‡ using benzene and silica gel at 15.25° C., cover the range of 2.26 — 59.65 mm. with 14 points; McBain, Lucas and Chapman,§ who "incline to regard the form and position of our sorption curves as being more typical of the true behaviour of charcoal towards vapours than those obtained in the best studies from other laboratories," have 16 points covering 11 to 255 mm. in the case of methyl alcohol on charcoal at 40° C. It is of interest to note that six of these points fall between 90 and 113 mm., and give evidence of a "break" in this region.

* *Loc. cit.*

† 'Z. Phys. Chem.,' vol. 132, p. 321 (1928).

‡ *Loc. cit.*

§ 'J. Amer. Chem. Soc.,' vol. 52, p. 2668 (1930).

Under these circumstances, it is not surprising that, when experimental results on adsorption are plotted, any deviations from a smooth curve are usually, explicitly or implicitly, ascribed to experimental error, however accurate the work in question claims to be. An examination of the literature of the subject will afford many illustrations. We need only mention earlier publications from this laboratory on the sorption of water vapour where, in quite a number of cases, points were found to fall off the "best" curve to a degree which it was difficult to account for at the time.*

Recently, a number of papers have appeared in which the authors have realised, in specific cases, the discontinuous nature of sorption phenomena. Simon† found discontinuities and stoichiometric relations in the sorption of various gases by dehydrated chabasite. Aharoni and Simon,‡ investigating the magnetic susceptibility of oxygen adsorbed by charcoal as a function of its concentration, found a sharp break at a certain point. Bull and Garner,§ determining the dependence on concentration of the differential heats of adsorption of oxygen and of nitric oxide on charcoal, found complex relations in both cases; above the lowest concentrations λ_0 , alternately rose and fell as the quantity of adsorbed oxygen increased, whilst nitric oxide gave a step-like curve, λ alternately remaining constant over appreciable ranges of q or falling. Benton and White|| obtained very well marked breaks in the isothermals given by hydrogen on reduced nickel at -183° and -191.5° C.

In all these cases the authors remark on their results and suggest some tentative explanation, such as the passage from a first to a second layer of adsorbed oxygen molecules (Aharoni and Simon), or the existence on the surface of the sorbent of areas of varying adsorptive activity (Bull and Garner; Benton and White). In a further case, that of some high pressure isothermals of gases on charcoal,¶ which show marked discontinuities,** the authors do not remark on the fact, and presumably ascribe the irregularities to experimental error. Possibly the inflections found by Polanyi and Welke†† at very low pressures in the isothermals of sulphur dioxide on a specimen of chemically activated charcoal at 0° and 5.3° C. are of the same nature.

* *E.g.*, 'J. Phys. Chem.,' vol. 33, pp. 1151 (fig. 2), 1682 (figs. 1, 2, 3), 1694 (fig. 1) (1929).

† 'Z. Elektrochem.,' vol. 34, p. 528 (1928); 'Z. Phys. Chem.,' vol. 132, p. 456 (1928).

‡ 'Z. Phys. Chem.,' B, vol. 4, p. 175 (1929).

§ 'Nature,' vol. 124, p. 409 (1929).

|| 'J. Amer. Chem. Soc.,' vol. 52, p. 2325 (1930).

¶ McBain and Britton, 'J. Amer. Chem. Soc.,' vol. 52, p. 2198 (1930).

** In particular see fig. 8 (*loc. cit.*).

†† 'Z. Phys. Chem.,' vol. 132, p. 371 (1928).

6. Discussion.

In addition to the specific suggestions just noted, the literature contains certain predictions of the possibility of discontinuous adsorption. Thus, Langmuir and Sweetser* point out that adsorption on plane surfaces consisting of more than one type of elementary space will occur in definite steps if there are marked differences between σ_1 , σ_2 , σ_3 , etc., the relative lives of the sorbed molecules on these spaces. Keyes and Marshall,† in discussing their work on the heat of adsorption of oxygen on charcoal, conclude that they are dealing with multimolecular layers, and point out that the ideal curve to be expected in this case would be discontinuous. In particular, Semenov‡ as a result of a discussion of the "critical condensation temperature" observed by workers with molecular rays, has come to the conclusion that a vapour whose ordinary heat of condensation exceeds its heat of adsorption as condensed film or two-dimensional liquid, will tend to be adsorbed discontinuously above the critical condensation temperature, with the formation of multimolecular layers. Amongst the reasons he gives for the non-observance of this phenomenon in practice are (1) insufficient accuracy of experimental work, and (2) inhomogeneity of adsorbing surface, which will result in the first formation of the two-dimensional liquid commencing at different points at pressures depending on the local adsorption potential.

The heats of adsorption of gases and vapours are usually greater than their heats of condensation to liquid; in such cases, Semenov's predictions should hold for temperatures *below* the "critical condensation temperature," and in this form correspond up to a point closely with our own present views.

A detailed presentation of these views at the moment would be premature for sufficiently obvious reasons. We will therefore merely outline them, dealing separately with charcoal and silica gel, and distinguishing between the behaviour of carbon tetrachloride, possibly typical of essentially non-polar sorbates, and that of water, probably an extreme case of those sorbates whose molecules are natural dipoles.

Adsorption by Activated Charcoals.—Activated charcoals have a very complex sub-microscopic structure, fully in accord with their microscopic appearance, and contain a large number of "active centres" (corners and edges of rudimentary crystals, projecting fragments of carbon chains, molecular cavities and clefts) of high adsorption potential. The first portions of vapour taken up

* 'J. Amer. Chem. Soc.,' vol. 40, p. 1361 (1918).

† 'J. Amer. Chem. Soc.,' vol. 49, p. 156 (1927).

‡ 'Z. Phys. Chem.,' B, vol. 7, p. 471 (1930).

are very strongly adsorbed and almost immobile on the surface. Even prolonged high temperature degassing *in vacuo* is relatively ineffective in removing such adsorbed material (*e.g.*, oxygen,* water,† carbon tetrachloride‡) and displacement by another adsorbed vapour is commonly more effective.§ This strongly held sorbate, poisons the charcoal to a certain extent for subsequent use.||

Most charcoals seem to take up water vapour in this region almost as well as they take up carbon tetrachloride, particularly when the less powerful displacing effect of water on adsorbed oxygen¶ is taken into account.

Such adsorption is identical with, or closely approaches "chemical" adsorption as pictured by Langmuir.

As the pressure in the vapour phase increases, chemical adsorption changes over to "physical" adsorption, in which van der Waals' forces are definitely predominant. The transition between the two types of sorption is, in all probability, a continuous one, corresponding to a gradual decrease in the degree of deformation of the sorbed molecules in the molecular field of the sorbent. In any case, the molecules adsorbed in this pressure region are progressively less firmly held than those bound at lower pressures, possess an increasing degree of mobility parallel to the adsorbing surface, and essentially constitute the two-dimensional gas phase of Volmer.**

We tentatively suggest this adsorption region in any given case to extend up to the pressure at which the first break is observed in our experiments, which, with activated charcoals, is apparently in the neighbourhood of 0.1 mm., and largely independent of the nature of the sorbate, of the exact charcoal used and of the temperature (between 25° and 100° C.). In this region, far more carbon tetrachloride than water is taken up.

Above 0.1 mm. pressure, we imagine the local formation of two-dimensional liquid (Semenoff) to commence in the neighbourhood of the different active centres, setting in at pressures determined by the local adsorption forces,

* Many authors.

† Allmand, Hand and Manning, *loc. cit.*, p. 1711.

‡ Harned, 'J. Amer. Chem. Soc.', vol. 42, p. 372 (1920); and our own observations.

§ Harned, *loc. cit.*; Allmand and Chaplin, *loc. cit.*

|| Lamb and Coolidge, 'J. Amer. Chem. Soc.', vol. 42, p. 1146 (1920); Coolidge, 'J. Amer. Chem. Soc.', vol. 46, p. 596 (1924); Allmand and Chaplin (*loc. cit.*). No such poisoning effect was observed by Goldmann and Polanyi (*loc. cit.*); they were using a chemically activated charcoal in which the most highly active centres are already poisoned by the activating agent.

¶ Allmand and King, *loc. cit.*

** 'Z. Phys. Chem.', vol. 115, p. 253 (1925).

this phenomenon being primarily responsible for the breaks observed.* Adsorption as two-dimensional gas will still continue, as the pressure increases, on such low potential portions of the surface as are not already occupied. In the case of carbon tetrachloride, we suggest that the processes thus outlined continue up to high pressures, if not to saturation, when the surface will be completely covered with a unimolecular liquid layer, in addition to which all minute cavities or clefts of suitable dimensions will be completely filled with liquid. This adsorbed layer will be under compression, and presumably the observations of Meehan† and of Bangham and Fakhoury‡ on the expansion of charcoal during adsorption are connected with this fact.

In the case of water vapour, we think that, whilst "primary" formation of two-dimensional liquid in the above sense is relatively unimportant, a further process, similar to the formation of the second, third and further layers postulated by Semenoff, sets in above a pressure which depends on the nature of the charcoal, and varies between 5 to 9 mm. at 25° C. Instead, however, of the formation of superposed multimolecular layers, we imagine that the "pools" of two-dimensional liquid water (*cf.* Goldmann and Polanyi, *loc. cit.*), which are primarily formed around the active centres, join up abruptly, producing particularly sharp breaks on the corresponding isothermals (as in fig. 1). The setting in of this process, not occurring with carbon tetrachloride, is responsible for the well-known sweep over of water vapour isothermals at intermediate pressures from low to high values of q , and we ascribe it essentially to the dipole nature of the water molecule, and to the tendency towards association thereby conferred. This tendency, reinforcing the weak attractive forces directly exerted by the charcoal, is sufficient at moderate pressures to hold water on a charcoal in the form of a discontinuous two-dimensional liquid film, which is probably far nearer to the unadsorbed liquid in its properties§

* We have found discontinuities in a carbon dioxide isothermal on charcoal at 40° C., i.e., above the critical temperature for carbon dioxide (experiment (viii)). According to Semenoff (*loc. cit.*), the critical temperature for a two-dimensional liquid film will be very low. On the other hand, Patrick, Preston and Owens, 'J. Phys. Chem.,' vol. 29, p. 241 (1925), conclude that the critical temperature of carbon dioxide adsorbed on silica gel is raised to at least 40° C.

† 'Proc. Roy. Soc.,' A, vol. 115, p. 199 (1927).

‡ 'Proc. Roy. Soc.,' A, vol. 130, p. 81 (1930).

§ The differential heats of adsorption (λ) of water vapour on charcoal in this pressure region are only very slightly greater than its heat of condensation ('J. Phys. Chem.,' vol. 33, p. 1692 (1929)); the water layer is presumably therefore under only slight compression. It is of interest to note that the general nature of the $\lambda - q$ relation found for water vapour on charcoal (*loc. cit.*, and Allmand and King, *loc. cit.*) is of the same nature as that described by Goldmann and Polanyi (*loc. cit.*) in other cases.

than is the case with non-polar sorbates such as carbon tetrachloride, and which becomes continuous at saturation.

We have suggested that the "primary" formation of two-dimensional liquid "pools" on activated charcoal is relatively unimportant in the case of water vapour. It is indeed possible that widely different adsorption mechanisms may ultimately be found necessary for substances like water and carbon tetrachloride. For we have found that, whereas a certain unactivated coconut charcoal is practically indifferent to the latter at 100° C., taking up 2 mg. per gram as compared with 140 to 240 mg. per gram taken up by steam activated specimens of the same material under the same pressure conditions, there is relatively very little difference between the quantities of water vapour taken up by the activated and unactivated charcoals at 25°.

A few further points should be noted. Whilst at one time imagining that there was a considerable degree of concordance between the values of the different pressures at which breaks were observed in our isothermals, we have never been able to detect any indication of regular relations between the Δq figures corresponding to adjacent breaks. In view of the nature of the suggested adsorption mechanism—simultaneous formation of gaseous and liquid films, with an additional process in the case of water—this is only to be anticipated. In addition, possible effects of incomplete displacement of oxygen must be reckoned with. It has been suggested that the breaks might disappear if this oxygen elimination were really complete. Our experimental results do not support this view.

A further objection to the proposed picture is that, considering the nature of the adsorbing surface, one would expect either far fewer or far more breaks than are actually found. To this we can only reply that we think it likely that, with more refined methods of measurement, the detailed structure of an isothermal would prove even more complex than is at present indicated.

Adsorption by Silica Gel.—We assume the adsorbing surface in this case to be far more uniform, and the active centres to be fewer and less potent. The nature of the surface—a dielectric with two essential atomic constituents in the lattice, and hence two possible types of elementary space, as compared with a conducting material with one essential atomic constituent in the case of charcoal—may also be of importance. In any case, in the region of relatively low pressures, whilst water vapour is more strongly adsorbed than it is by charcoal, the reverse is the case for carbon tetrachloride, the result being that the quantities taken up are of the same order. At very low pressures, on the

other hand, water vapour is far more powerfully held than is carbon tetrachloride; the case is one of "chemical" adsorption.

We suggest the same qualitative picture at higher pressures as for charcoal. Owing to the absence of highly active centres, silica gel is a relatively poor adsorbent of non-polar molecules under these conditions; on the other hand, the abrupt sorption of larger amounts of water* at intermediate pressures is still more marked than is the case with charcoal (fig. 10). We agree that it is difficult to distinguish between capillary condensation (Zsigmondy; Patrick) and the sudden formation of the two-dimensional liquid which we prefer, and would only remark that, if the former explanation be correct (1) the Kelvin vapour pressure formula can nevertheless hardly hold, except at high p/p_0 values, (2) the difference between the types of curve shown by benzene and by water requires explanation, (3) as also do the facts that a sugar charcoal, without any morphological pores, furnishes the same general type of water vapour isothermal as do other charcoals and silica gel,† whilst giving a benzene isothermal showing marked discontinuities.

Conclusion.—Our views as a whole will be seen to have much in common with those of Goldmann and Polanyi and of Semenoff. More, and more exact, work, with a rigid control of variables, will be required before further elaboration is possible. It is unnecessary to detail the many points which call for investigation or confirmation.

It may, however, be pointed out that the experimental results recorded, whilst showing the non-applicability to a complex porous sorbent like charcoal of any general adsorption formula which purports to cover a wide range of experimental data, in no sense affect deductions drawn for plane surface conditions, and make it even clearer than before that only experimental work with plane, or relatively plane, surfaces is likely to yield information of value on the fundamental adsorption processes.

Summary.

1. The results of earlier work pointing to discontinuities in the process of the sorption of vapours by charcoal are reviewed.

2. The results of the detailed investigation by means of a simple static technique of eight new isothermals are communicated. They include measure-

* SO_2 and NH_3 , both natural dipoles, give isothermals on silica gel resembling those of benzene rather than those of water.

† 'J. Phys. Chem.' vol. 33, p. 1667 (1929).

ments with (a) four different charcoals, and (b) with five different condensable vapours and with carbon dioxide.

3. The results of the examination, by two different methods, of three vapour isothermals on silica gel are communicated.

4. All these isothermals show evidence of discontinuity, sometimes very marked, sometimes barely exceeding the limits of experimental error.

5. Mention is made of recent similar results of other observers.

6. Suggestions are made with a view to explaining the above facts.

Examples of the Uncertainty Principle.

By C. G. DARWIN, F.R.S., Edinburgh University.

(Received December 17, 1930.)

1. In the general synthesis of classical dynamics with the quantum theory, the Uncertainty Principle* plays a most useful part. It is of course only one aspect of the new mechanics, but it is a very helpful one since by its means it becomes easy to see where the old classical ideas broke down. The state of affairs in the quantum theory is not unlike that of the early days of relativity, when most of those who studied the subject felt the need of supporting the formal theory by seeing how the old ideas failed in specific cases. Here the formal theory is very abstract and is not easy to follow intuitively, and the Uncertainty Principle plays much the same rôle as did the examples of clocks and rods in relativity theory. For this reason it is more appropriate for illustrative examples, than for any extreme generality, and though a number of examples have been already given by Heisenberg and Bohr,† it may not be amiss to have some more. There are probably some who will have shared my experience that it is often by no means easy to detect how the uncertainty enters into a given experiment, though once detected the arguments are usually very simple. In a recent conversation Professor Bohr criticised some rather careless remarks that I had made,‡ and the present work was undertaken

* Heisenberg, 'Z. Physik,' vol. 43, p. 172 (1927).

† See, for example, Heisenberg, "The Physical Principles of the Quantum Theory," chap. 2.

‡ "Discussion on Magnetism," 'Lond. Phys. Soc.,' vol. 42, p. 362. I attributed to him a theorem concerning the magnetic moment of the free electron which was different

to clear matters up. It may be shortly described as a study of the Uncertainty Principle in connection with electrometers and magnetometers.

It may be of interest to point out that the Uncertainty Principle can be regarded from a rather different aspect. The "resolving power" of optical instruments was discussed very fully by Rayleigh on wave principles, but as long as matter was regarded in the classical manner, a mechanical instrument could be considered as capable of measuring quantities with absolute accuracy. Now that we know that matter also has wave properties, there is need of a theory of the resolving power of mechanical instruments, and this is exactly what the Uncertainty Principle supplies.

The methods involved in the use of the principle may be recalled by citing Heisenberg's original example, in which he considers how the position of an electron could be fixed with the help of a microscope. He starts with the idea of an electron as a particle, say, at rest at a definite point. To fix this point to precision Δx , he must have light of a wave-length at least as short as Δx . It is wave principle that gives this, but the light is now regarded as a particle and as such has momentum of order $h/\Delta x$. When it is scattered into the microscope, part of this momentum is communicated to the scattering electron, so that the electron's momentum is changed in the act of observing its position. An essential part of the argument is that a microscope requires convergent light, since this makes it uncertain in what direction the light-quantum was going when it struck the electron; otherwise the nature of the collision would be known, and though the electron had changed its motion, it would have done so to a calculable degree, and there would be no uncertainty. All arguments illustrating the principle have similar characteristics. They start with the pure particle aspect, assuming that position and momentum are both given, or some other pair of dynamically conjugate quantities. They then somehow make use of wave principles, perhaps through the idea of resolving power, or else simply of diffraction, and then show how the observing instrument so reacts on the object as to spoil the initial assumptions. An essential point in the process is to see why the reaction is indeterminate, for if it were definite some device could be introduced to compensate for it.

2. Consider the following problem. An electron (or any particle of known from that which he had maintained. When he established that the moment could not be detected by a magnetometer, he did not need to make any appeal to the reaction of the magnetometer, and I suggested that the conditions would be altered by the simultaneous use of several magnetometers. It is shown in § 5 that when the reaction is allowed for, the new experiment is no more competent than the old to measure the moment, and there is thus complete agreement with Bohr's theorem.

charge) is free on a certain line, but at rest. We have an electrometer at some fixed point on this line, with which we measure the electric force from the electron, and from this we calculate its position. We want to see how we are prevented from doing the experiment with infinite accuracy. To do this we must consider the resolving power of electrometers, and the easiest way of estimating the resolving power of any instrument is to take advantage of the well-known theorems of optics on the subject. We therefore choose an optical electrometer, for which the estimation is simple. A possible way of measuring electric fields is to observe the Stark effect* that they produce. No restriction whatever is placed on the magnitude of the Stark effect, and so we may expect that it will represent the resolving power of other electrometers also. Our electrometer is thus a spectrum tube emitting lines which show the Stark effect, and we measure the displacement of one of these. Suppose that the line in question is associated with the two energy levels $W_1 + M_1 E \rightarrow W_2 + M_2 E$, where E is the field to be measured. If we want to measure E to accuracy ΔE , we must be able to distinguish between two frequencies differing by $(M_1 - M_2) \Delta E / h$. To do this it will be necessary for their phases to accumulate a difference of something like a complete cycle, and this will take a time $\Delta t > h / (M_1 - M_2) \Delta E$. This argument is, of course, nothing but an elaboration of Heisenberg's relation $\Delta W \Delta t > h$. It fixes the resolving power of the electrometer.

We have now done with the essential appeal to wave theory, and for the rest may consider only the particle aspect, not only for the electron, but also for the radiation of the light from the spectrum tube. We want to reduce the reaction of the electrometer to the least possible, and so we suppose it to contain only one atom which is in level 1 at the beginning and in level 2 at the end of the experiment. At some unknown time during Δt the electrometer-atom switches over from state 1 to state 2. We must consider how it reacts on the free electron; the effect is produced because the atom has an electric moment. We might at first sight ask why it should not be possible to compensate for this moment by means of some permanent static field, but a little consideration shows that it cannot be done. The moment is M_1 if the atom is in the upper level, and M_2 if in the lower. The free electron is thus part of the time under the influence of M_1 and part under M_2 , and we cannot know when the switch occurs, so that it is impossible to know how much time to allow for each. The best compensation we can make is to super-

* Bohr has proposed the use of the Zeeman effect for a magnetometer, and this is an obvious extension.

pose a permanent field equivalent to $\frac{1}{2}(M_1 + M_2)$; then if the switch occurs at the start there will be a residual moment of $\frac{1}{2}(M_2 - M_1)$, and if at the end of $\frac{1}{2}(M_1 - M_2)$, and the average value may be anything between these two. We conclude that the electrometer must have a moment M , of order not less than $M_1 - M_2$, but uncertain to this degree. The rule that there can be no observation without uncertainty is illustrated by the lines for which $M_1 = M_2$. For these the reaction could be compensated, but these are just the lines which fail to show the Stark effect, and so are useless for an electrometer.

It is now easy to exhibit the way the Uncertainty Principle works. We propose to fix the position of the electron to accuracy Δx . Reckoning only to orders of magnitude, this requires us to measure the force to accuracy $e\Delta x/r^3$, where r is a rough value of the distance. To do this will take a time $\Delta t > \hbar r^3/(M_1 - M_2)\Delta x$. During this time the electron is under the influence of a moment from the electrometer, of uncertain magnitude M which cannot be reduced below the order $M_1 - M_2$. The resultant electric force is of order M/r^3 , yielding a mechanical force eM/r^3 . In time Δt this produces a change in momentum

$$\Delta p = \frac{eM}{r^3} \Delta t > \frac{\hbar}{\Delta x} \frac{M}{M_1 - M_2}.$$

This is equivalent to saying that the momentum is changed by an uncertain amount at least as great as $\hbar/\Delta x$ during the experiment, which is exactly the Uncertainty Principle.

A slight generalisation will show how the result is related to the well-known reciprocal relations of classical dynamics. Imagine that the electron is free to move along a line x , while the electrometer is now anywhere in space and measure the force in an arbitrary direction X . Then if r is the mutual distance, the force to be measured is $e \frac{\partial}{\partial X} \frac{1}{r}$. If the electron is to be found to accuracy

Δx , the force must be measured to accuracy $\Delta x \cdot e \frac{\partial^2}{\partial x \partial X} \frac{1}{r}$ and this will take

a time $\hbar / \left\{ (M_1 - M_2) \Delta x \cdot e \frac{\partial^2}{\partial x \partial X} \frac{1}{r} \right\}$. On the other hand the potential of

the electrometer is $M \frac{\partial}{\partial X} \frac{1}{r}$, and the mechanical force on the electron in its

direction of freedom is $eM \frac{\partial^2}{\partial x \partial X} \frac{1}{r}$, so that the change of momentum is

$$\Delta p = eM \frac{\partial^2}{\partial x \partial X} \frac{1}{r} \cdot \Delta t$$

and we get the same result as before.

3. We now consider a similar problem for magnetic fields, this time using the generalised Zeeman effect as magnetometer. We will suppose that an electron (without spin) is moving along the x -axis in a known position with velocity approximately u . A magnetometer is installed at the point $(0, a, 0)$ so as to measure the component along z . The symbols M , etc., now represent the magnetic moment of the magnetometer-atom. The magnetic force on the magnetometer is $H = \frac{eu}{c} \frac{a}{r^3}$, where $r = \sqrt{(a^2 + x^2)}$ is the distance. We are supposing r known; it will, of course, vary during the experiment, but in a manner that could be allowed for with sufficient approximation. We are to measure u to accuracy Δu , and this means measuring H to accuracy $ea\Delta u/cr^3$, which will take a time $\Delta t > cr^3h/(M_1 - M_2)ea\Delta u$. This is just as before, but the reaction arises in a different way. The mechanical force due to M is at right angles to both the magnetic force and the velocity, and so is perpendicular to the line on which the electron is constrained to move; it is thus without effect. But we must remember that during the time of the experiment the magnetometer's moment changes from M_1 to M_2 , and this change will give rise to electromagnetic induction. The moment M gives vector potential with x -component Ma/r^3 at the electron and so there is an electric force $\frac{1}{c} \frac{dM}{dt} \frac{a}{r^3}$. Integrating over the time Δt this will produce a change of momentum during the interval of amount $\frac{e}{c} (M_1 - M_2) \frac{a}{r^3}$. There is no uncertainty in this; the uncertainty enters because the change occurs impulsively at the moment of the switch from M_1 to M_2 , and we cannot know when this happens. Thus if the impulse is given early, the electron will move further in consequence, than if it is given late. So there will be an uncertainty in position of amount $\frac{e}{mc} M \frac{a}{r^3} \Delta t$, where M is again of the magnitude of $M_1 - M_2$. Substituting for Δt , we find $\Delta x > h/m \Delta u$.

4. We next consider the orientation of the magnetic moment of an electron, regarding it as fixed in position, as it would be for example in an alkali atom. The electron is at distance r from the magnetometer and its moment is $\mu = eh/2mc$, so that the force to be measured is of magnitude μ/r^3 . If the experiment is to be of any use we must have better precision than this; let us aim at measuring $\kappa\mu/r^3$, where κ is a fairly small fraction. The experiment must then take a time greater than $\Delta t = r^3h/(M_1 - M_2)\kappa\mu$. The reactive force is M/r^3 , where M is uncertain but of the same magnitude as $M_1 - M_2$.

This force will cause a precessional motion of the electron at twice the rate of the Larmor precession, that is with angular velocity $\frac{e}{mc} \frac{M}{r^3}$, and so in time Δt it will precess through angle $\frac{e}{mc} \frac{M}{r^3} \Delta t$ which is of the order of $1/\kappa$. This means that the electron will have precessed at least several times round, and will end pointing in an arbitrary azimuth. All that can be determined therefore is the component along the axis of the precession. This last result is, of course, also true in the classical theory by virtue of the reciprocal relations of dynamics. For if μ is the vector moment and x the position of the magnet, $\left(\mu, \frac{\partial}{\partial x} \frac{1}{r}\right)$ is the potential of its force, and if X is the line of the magnetometer, then the force measured is $\left(\mu, \frac{\partial^2}{\partial X \partial x} \frac{1}{r}\right)$. On the other hand the reaction has potential $M \frac{\partial}{\partial X} \frac{1}{r}$, and so the reactive force is the vector $M \frac{\partial^2}{\partial x \partial X} \frac{1}{r}$. The scalar product of this by μ is just what the magnetometer measures, and it only depends on the component of μ in the direction of the reactive force.

The new feature is that the magnetometer, in fixing this component, has spoilt that at right angles. We can thus see that it is impossible ever to determine the components of magnetisation of the electron in two perpendicular directions simultaneously by the use of two magnetometers; for the electron will be precessing through arbitrary angles about the two axes at the same time and so will end in a quite arbitrary direction. This is a well-known property of spatial quantisation, connected with the fact that the components of angular momentum in perpendicular directions do not commute. The same result is true for the moment of a whole atom, and indeed for any system for which the precessional rate under force H bears a proportion of order $H/\hbar$ to the magnetic moment.

5. The important question of the magnetic moment of the *free* electron was discussed by Bohr.* The magnetic force that it exerts will depend on its position and velocity as well as on the moment, and to observe the last we must know the effects of the other quantities. Bohr imagined that a previous unspecified experiment had fixed the position and velocity, of course with the appropriate uncertainty. The electrons might for example have been liberated from a slit after falling through some definite voltage; this would, of

* Mott, 'Proc. Roy. Soc.,' A, vol. 124, p. 422, see Appendix, p. 440.

course, give them uncertainties of position and speed obeying $\Delta x \Delta u > h/m$, etc. The force due to the current is then of order eu/cr^2 , and is therefore uncertain to order $e\Delta u/cr^2$, which is greater than $eh/mcr^2\Delta x$, and so much greater than eh/mcr^2 , which is the whole force due to the moment.

Now it might seem that not all the possibilities have been exhausted by this argument. For example, by using two magnetometers simultaneously on opposite sides of the electron, it is easy to separate the current-force from the moment-force. We might think that though the uncertainty of velocity is so great as to mask the force on a single instrument, yet it will be the same uncertainty for both, and so could be determined and thereby eliminated. It was, of course, never anticipated that this would be so, but the present work was primarily undertaken to see why it is not. We shall therefore design a self-contained experiment, from which, assuming infinite resolving power and no reaction, it would be possible to evaluate position and velocity as well as moment.

We take a given direction for the moment, say along z . There are then seven unknowns, the position x, y, z and velocity u, v, w of the electron, and the magnitude of its moment. The force in the z -direction at a distant point $(R \cos \phi, R \sin \phi, 0)$ is found to be

$$\frac{e}{c} \left\{ \frac{1}{R^2} (v \cos \phi - u \sin \phi) + \frac{1}{2R^3} [(xv - yu) + 3 \cos 2\phi (xv + yu) + 3 \sin 2\phi (yv - xu)] \right\} - \frac{\mu}{R^3}.$$

As this does not contain z or w , we conclude that a set of five magnetometers in the plane of xy will suffice. It does not matter how they are disposed, but for symmetry we may put them at the corners of a regular pentagon. If we denote the five measurements by $H_1, H_2, \dots$, we can obtain equations

$$\begin{aligned} \frac{e}{cR^2} (xv - yu) - 2 \frac{\mu}{R^3} &= \frac{2}{5} \sum_{n=1}^5 H_n, & \frac{e}{cR^2} v &= \frac{2}{5} \sum_{n=1}^5 H_n \cos \frac{2\pi n}{5}, \\ \frac{2}{5} \frac{e}{cR^2} (xv + yu) &= \frac{2}{5} \sum_{n=1}^5 H_n \cos \frac{4\pi n}{5}, & -\frac{e}{cR^2} u &= \frac{2}{5} \sum_{n=1}^5 H_n \sin \frac{2\pi n}{5}, \\ \frac{2}{5} \frac{e}{cR^2} (yv - xu) &= \frac{2}{5} \sum_{n=1}^5 H_n \sin \frac{4\pi n}{5}, \end{aligned}$$

and it is evident that these can be solved for x, y, u, v and μ . Thus our experiment would work, given infinite resolving power. It may be thought trivial to go into so much detail over the matter, but the whole subject is full of pitfalls

and it is prudent always to examine a proposed experiment so as to be sure that it works.

Now apply the argument of § 3. The magnetometer at ϕ has vector potential with components $\frac{M}{R^2} \sin \phi$, $-\frac{M}{R^2} \cos \phi$ near the origin, and so gives an impulse

$\frac{e}{c} \frac{(M_1 - M_2)}{R^2}$ to the electron at some time during the experiment. All five do

this, and since we have supposed that the impulses are in directions at five equal angles, it happens that the final velocity will be the same as the original. But the times at which the impulses act are quite uncorrelated, so that the electron will have moved its position by an amount uncertain to order

$\frac{e}{mc} \frac{M}{R^2} \Delta t$. Taking Δt just so long that we shall be able to detect the moment-

force, we have a shift of position of order $\frac{e}{mc} \frac{M}{R^2} \cdot \frac{\hbar R^2}{(M_1 - M_2) \mu}$ or R . This

means that any magnetometer exerts such a reaction on a free electron, that it drives it right away in a shorter time than is necessary in order to resolve the magnetic force due to the moment. This is Bohr's result and we see how again the Uncertainty Principle asserts itself.



*The Kinetics of the Combination of Hydrogen and Oxygen: the
Influence of Iodine.*

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Introduction.

The experiments to be described in this paper are based on the observation of H. B. Dixon that iodine raises the ignition temperature of hydrogen in oxygen. The study of its influence on the slow combination of these gases promised to throw additional light on the nature of the reaction chains by which the change takes place.

Since a number of facts relevant to the investigation are contained in recent publications in a rather unco-ordinated way, it will be well to begin by bringing them together. They may be summarised as follows:—

- (1) Below about 520° C. in vessels of porcelain or silica the combination of hydrogen and oxygen occurs mainly on the surface of the vessel, and is approximately of the first order.*
- (2) As the temperature is raised from 520° C. to 600° C., and especially as the pressure is raised, a high-order gas reaction comes into prominence. Under some conditions its rate may be nearly proportional to the cube of the hydrogen concentration, and to a power of the oxygen concentration greater than the first. It is accelerated by steam and other chemically indifferent gases, and retarded in an extremely marked degree by reduction of the dimensions of the vessel.*†
- (3) At relatively low pressures an entirely new phenomenon appears; there is an upper and a lower limit of pressure above and below which the reaction is quite slow, and between which explosion occurs.‡
- (4) The upper limit is displaced in the direction of higher pressures by increase of temperature; the lower limit is slightly lowered. Argon lowers the partial pressure of hydrogen and oxygen at the upper limit.

* Bone and Wheeler, 'Phil. Trans.,' A, vol. 206, p. 1 (1906); C. N. Hinshelwood and H. W. Thompson, 'Proc. Roy. Soc.,' A, vol. 118, p. 170 (1928). (References to the earlier work of Bodenstein are given here.)

† C. H. Gibson and C. N. Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 119, p. 591 (1928).

‡ Thompson and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 122, p. 610 (1929); Kopp, Kovalsky, Sagulin and Semenov 'Z. Phys. Chem.,' B, vol. 6, p. 307 (1930).

The upper limit is not much affected by the dimensions and nature of the vessel.

- (5) In presence of small amounts of nitrogen peroxide hydrogen and oxygen may explode at temperatures more than 100° C. lower than normally. There are two critical concentrations of nitrogen peroxide above and below which reaction is negligible and between which explosion occurs. The limits are quite sharp.*
- (6) When crossed streams of hydrogen and oxygen meet in an atmosphere of nitrogen at partial pressures and temperatures such that the low pressure explosion would occur in a silica or porcelain vessel, no flame appears at the region of intersection of the streams. If, however, a quartz or porcelain rod is brought into this region ignition occurs.†
- (7) According to Alyea and Haber, the ease of ignition, in the low pressure region, of mixtures of hydrogen and oxygen streamed through narrow porcelain tubes is much greater when the tube has been "pre-treated" with oxygen than when it has been "pre-treated" with hydrogen.

With regard to the interpretation of these facts, (1) requires no further comment.

(2) shows that the gas reaction is a chain reaction in which the chains are broken principally at the wall of the vessel. As far as the influence of the vessel size on the rate of reaction is concerned, they might also start on the wall, since, if they traversed the gas before meeting the wall again, the rate would increase with increasing vessel size in the manner actually found. But the high order of the reaction suggests that the chains are actually initiated in the gas (Gibson and Hinshelwood suggested ternary collisions $2\text{H}_2 + \text{O}_2$, giving excited molecules of steam).

With regard to (3), two kinds of mechanism might give rise to the existence of such limits: (a) A heterogeneous reaction might be occurring, the rate of which first increased and then decreased again as the pressure increased—a type of surface reaction by no means unknown. Between two limits of pressure, therefore, this reaction might be generating heat at certain points on the surface rapidly enough to ignite the gas as a whole.‡ This hypothesis is disproved by

* Gibson and Hinshelwood, 'Trans. Faraday Soc.', vol. 24, p. 559 (1928); Thompson and Hinshelwood, 'Proc. Roy. Soc.', A, vol. 124, p. 219 (1929).

† Alyea and Haber, 'Z. Phys. Chem.', B, vol. 10, p. 193 (1930).

‡ Gibson and Hinshelwood, 'Trans. Faraday Soc.', vol. 24, p. 559 (1928).

the fact that the rate of the surface reaction does not vary with the pressure in anything like the required manner, showing no sign whatever of increasing as the pressure drops from higher values towards the explosion limit. To make the theory fit the facts it would be necessary to postulate the existence of special active centres on the surface with appropriate properties. (b) A hypothesis* which at present appears satisfactory is that of branching chains, which are prevented from multiplying indefinitely by deactivation at the wall below the lower limit, and by deactivation in the gas above the upper limit, but leading to explosion between these limits. The facts mentioned under (4) are consistent with the hypothesis that the upper limit is determined by deactivation in the gas phase.

One of the more striking characteristics of the whole phenomenon is that the mechanism by which chains are propagated in the explosion region at low pressures appears to be independent of that by which they are propagated at higher pressures.

(5) will be referred to below.

(6) is evidence that the chains concerned in the low pressure process start at the wall of the vessel, but gives no reason to doubt that the upper limit is chiefly determined by breaking of branching chains in the gas phase. Alyea and Haber themselves in their latest communication neither accept nor reject the branching chain hypothesis.

Taking all the facts into consideration, it appears to us most probable that in the low pressure region chains are propagated through the gas, but are initiated by centres which perhaps must be formed heterogeneously; at the lower limit surface deactivation plays the important part in stopping the chains, at the upper limit gas deactivation. In the region of higher pressures chains of somewhat different kind start in the gas and terminate at the wall.

(7) would apparently result from adsorption hysteresis which influences the heterogeneous production of the centres from which the chains start; it appears later in this paper that the effect is not a very pronounced one.

With regard to the chemical processes occurring in the chains in the low pressure region, Thompson and Hinshelwood supposed primary formation of hydrogen peroxide, which reacts with hydrogen to give two excited molecules of steam. These hand on their energy, activating oxygen or hydrogen which forms more hydrogen peroxide. Nitrogen peroxide can also initiate

* Thompson and Hinshelwood, *loc. cit.* For general theory of branching chains see Semenov, 'Z. Physik,' vol. 46, p. 109 (1927).

chains. The chains are broken either at the surface, or by one of the processes :—



or by deactivation of active molecules in " collisions of the second kind " with inert gas molecules.

In the light of (6) above it would be necessary to suppose the first H_2O_2 molecules to be formed at the surface. Haber and his collaborators† prefer to regard the chains as starting by the process $\text{H}_2 + \text{O}_2 = 2\text{OH}$, followed by $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$. They base this theory upon the existence of the OH bands in the emission spectrum of hydrogen-oxygen flames, and in the absorption spectrum of steam at 1200°C .; and upon thermochemical data which show the reactions in question to be possible ones. On the other hand, it must be remarked that hydrogen peroxide can be condensed out at ordinary temperatures from flames, and that 1200°C ., where the OH absorption bands appear, is as much above the normal reaction temperature (550°C .) as " ordinary temperatures " are below it. The existence of the equilibrium $2\text{OH} \rightleftharpoons \text{H}_2\text{O}_2$ makes it possible that the two views of the matter are not incompatible. Finally, however, since inert gases such as argon and, as shown later, steam lower the upper explosion limit, they evidently have a deactivating influence, which is more easily understood as occurring in collisions with excited molecules than in collisions with free atoms or radicals. If the initial process is $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$ it is understandable that it should have to occur in contact with the vessel wall, since processes of the type $\text{A} + \text{B} = \text{AB}$ require the participation of a third body in order that the quantum conditions may be consistent with the mechanical conservation laws. On the other hand, if it is $\text{H}_2 + \text{O}_2 = 2\text{OH}$ there would be no such necessity.‡

The matter must be left open until further data are forthcoming, but it is

* Schumacher modifies this view of the matter by assuming that, at the upper limit of nitrogen peroxide concentration, the reaction $\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$ removes oxygen atoms which below the limit start chains by the process $\text{H}_2 + \text{O} = \text{OH} + \text{H}$ ('Nature,' vol. 126, p. 132 (1930)). Farkas and Harteck object to this on the ground that oxygen atoms produced photochemically do not cause explosion. They prefer the original explanation of Gibson and Hinshelwood that the nitrogen peroxide at the upper limit poisons the wall reaction which might otherwise set up chains. Thompson and Hinshelwood, finding that the upper limit, in the absence of nitrogen peroxide, could not be explained in this way, suggested, as more coherent, the explanation based on the mutual destruction of the peroxide molecules.

† Bonhoeffer and Haber, 'Z. Phys. Chem.,' vol. 137, p. 263 (1928).

‡ This point arose from a discussion of the matter with Professor G. I. Finch.

perhaps permissible to say that the existing differences of opinion* relate rather to matters of detail than to the general interpretation of the reaction in terms of the chain mechanism.

The experiments now to be described deal primarily with the influence of iodine and water vapour on the combination in silica and porcelain vessels.

Iodine retards the gaseous reaction, inhibits the low pressure explosion, but accelerates the surface reaction. Water vapour inhibits the explosion, if present in great enough amount; such amounts, as shown previously, would accelerate the high pressure gas reaction by an "inert gas" effect.

Certain other matters, amplifying points dealt with in the foregoing introduction are, however, first dealt with.

Question of Negative or Positive Catalysts in Commercial Hydrogen.

The apparatus used was similar to that already described; the reactions took place in bulbs of silica or porcelain, and the rate of reaction was measured manometrically. Pure oxygen was prepared from potassium permanganate. Hydrogen was obtained from a cylinder of electrolytic hydrogen, dried by means of phosphorus pentoxide, and then used without further purification.

The reaction between hydrogen and oxygen is shown in the sequel to be sensitive to the presence of certain inhibitors. It is important to know whether cylinder hydrogen contains impurities which can act in this way. The behaviour of this hydrogen was compared with that of pure hydrogen, admitted into the reaction vessel through a hot palladium valve. The differences found were not greater than differences which might arise from the uncontrollable variability of the bulb surface. This justified the use of unpurified cylinder hydrogen in the rest of the investigation.

Comparison between Cylinder Hydrogen and Pure Hydrogen.

Unpacked silica bulb. $H_2 = 200$ mm., $O_2 = 100$ mm.

Experiments tabulated in order as performed.	Times required for 25 per cent., 50 per cent. and 75 per cent. of complete reaction.		
	t _{25 per cent.}	t _{50 per cent.}	t _{75 per cent.}
Pure hydrogen	3 0	6 20	13 57
Cylinder hydrogen	4 18	7 40	13 23
Pure hydrogen	4 18	8 8	15 20
Cylinder hydrogen	4 7	7 17	12 20

* Another variant of the mechanism, based upon initial production of atomic hydrogen, is discussed by Semenov, 'Z. Phys. Chem.,' B, vol. 2, p. 161 (1929).

Effect of "Pre-treatment" of Vessel with Hydrogen or Oxygen.

A series of experiments was carried out to determine whether the upper limit of the low pressure explosion region depended on the order in which hydrogen or oxygen was let into the reaction bulb. In each experiment the bulb was first evacuated, then 100 mm. of one gas were let in ; after 2 minutes this was pumped out ; this process was repeated. Then a suitable pressure of the same gas was let in, followed by the equivalent amount of the other gas. The mixed gases were then slowly drawn out of the bulb, and the pressure at which explosion occurred was measured.

With an unpacked silica bulb, no regular differences were found, as shown below ; the order in which the experiments were made is indicated :—

Effect of "Pre-treatment" on Explosions in Silica Bulb at 524° C.

	Explosion pressures.				
Hydrogen admitted first.....	(1) 73		(3) 77		(5) 76*
Oxygen admitted first.....		(2) 77		(4) 77	

Small differences were found with the porcelain bulb, as shown below :—

Effect of "Pre-treatment" on Explosions in Porcelain Bulb at 508° C.

	Explosion pressures.					
Hydrogen admitted first.....	(1) 62		(3) 61		(5) 60	(7) 61*
Oxygen admitted first.....		(2) 65		(4) 66	(6) 66	

* These pressures differ by about 20 mm. from those recorded by Thompson and Hinshelwood. A few measurements, however, made at higher temperatures before prolonged exposure of the vessel to iodine vapour, agreed quite well with the earlier results. This itself suggests a "pre-treatment" effect. Unfortunately, however, a change in the zero of the pyrometer which occurred during the present series of experiments makes it impossible to be certain that some of the difference is not due to an error in the absolute temperatures recorded. It should be remarked that the relative values and the constancy of the temperatures are beyond doubt. For any other purposes of this paper the *absolute* temperature values are irrelevant.

These results, as far as the direction of the effect goes, agree with the observations of Alyea and Haber, but the magnitude of the effect appears to be much smaller than would be gathered from their account.

Influence of Water Vapour on the Upper Explosion Limit.

The effect of the presence of water vapour in the hydrogen-oxygen mixture on the upper explosion limit was investigated in the porcelain bulb at 514° C. The results, given below, are somewhat erratic, but show definitely that a sufficiently large percentage of water vapour lowers the partial pressure of $2\text{H}_2 + \text{O}_2$ at the upper limit, and that a still larger percentage stops the explosion altogether. The explosion limit was found by the usual "withdrawal" method.

Influence of Water Vapour on Low Pressure Explosions.

(Porcelain bulb at 514° C.)

Amount of water vapour as percentage of total pressure.	Partial pressures at upper explosion limit (in millimetres of mercury).		
	P_{total}	$P_{\text{H}_2\text{O}}$	$P_{(\text{H}_2 + \text{O}_2)}$
0	69	0	69
0	66	0	66
0	66	0	66
2.0	63	1.25	62
3.2	65	2.1	63
6.2	64	4.0	60
8.8	59	5.2	54
11.3	53	6.0	47
13.1	65	8.5	56.5
16.0	61	9.75	51
22.7	33	7.5	25.5
35.9	No explosion.		

Incidentally it is to be noted that the influence of water vapour is much too small to have modified the normal explosion pressures determined by the "withdrawal" method; a question raised by Semenov. In previous experiments it has been found that water vapour somewhat retards the surface reaction; and accelerates the gas reaction at higher pressures, in the same way as an inert gas, that is, by hindering the diffusion of the chains to the walls.

The Influence of Iodine.

Iodine was introduced into the reaction vessel as isopropyl iodide, which instantly decomposed into propane, propylene and iodine:



Thus the actual iodine pressure in the reaction vessel is equal to one-third of

the measured pressure. Larger amounts were measured in directly, and smaller amounts after suitable dilution with known amounts of hydrogen.

It is shown later that all the effects observed were due to the iodine, and not the hydrocarbons.

The effects of iodine are as follows :—

- (1) The explosion which normally takes place when the pressure is reduced below the upper critical limit does not take place when iodine is present in concentration greater than a certain minimum amount. This was observed in unpacked silica bulbs, a tube-packed silica bulb and a porcelain bulb. The effect was investigated in detail in a large silica bulb. Amounts slightly less than are required to stop the explosion altogether lower the explosion pressure.

Influence of Iodine on Upper Explosion Pressure.

(Unpacked silica bulb at 520° C.)

Order of experiment.	Amount of iodine as percentage of total pressure.	Explosion pressure (in mm. of mercury).
2	0·057	No explosion
3	0·011	No explosion
7	0·0057	No explosion
8	0·0022	No explosion
9	0·0022	No explosion
6	0·0011	50
10	0·0011	21
5	0·00011	51
1	0	72
4	0	74

- (2) The surface reaction is accelerated by iodine.

- (3) The high pressure gas reaction is inhibited.

These facts were established by comparing the reaction in bulbs of widely different dimensions and surface-volume ratios.

In an unpacked bulb at relatively high temperatures and pressures the gas reaction tends to predominate; under these conditions addition of iodine retards the reaction very markedly. In such a vessel an acceleration is observed only at relatively low temperatures and pressures.

Influence of Iodine on Gas Reaction.

(Unpacked silica bulb at 550° C. $H_2 = 300$ mm., $O_2 = 150$ mm.)

Concentration of iodine (mm.).	Rate of reaction (mm. pressure change per min.).
0	35
0.0033	14
0.017	5.4
0.033	5.0
0.10	5.4
0.17	5.2
0.33	6.3
0.83	8
1.33	11.4

These are plotted in fig. 1. Small amounts of iodine produce the maximum retardation. The increase in rate which occurs when the minimum is passed must be due to the acceleration of the surface reaction.

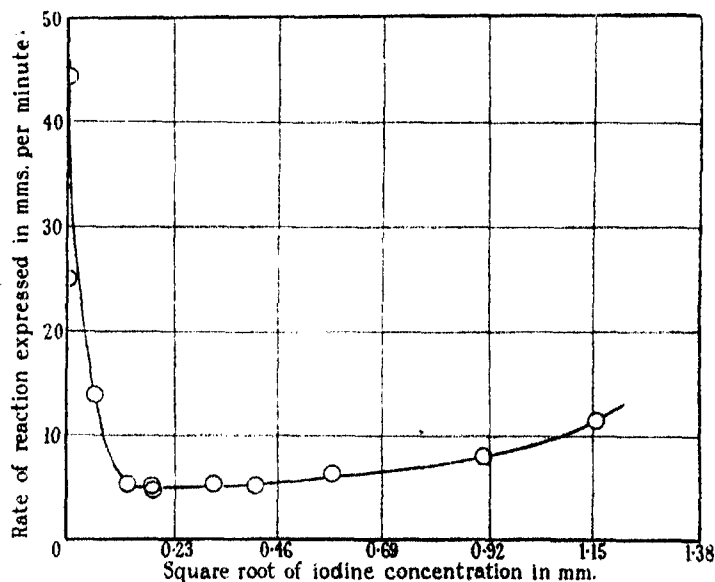


FIG. 1.—Inhibition of Gaseous Reaction by Iodine.

In a bulb packed with spheres of silica the surface reaction tends to predominate, and only acceleration by iodine is observed even at relatively high temperatures.

Influence of Iodine on Surface Reaction.

(Sphere-packed silica bulb at 600° C. $H_2 = 400$ mm., $O_2 = 200$ mm.)

Concentration of iodine (mm.).	Rate of reaction (mm. pressure change per min.).
0	10.5
0.3	36.5
1.33	51.8
3.33	75
6.66	94

These results are plotted in fig. 2, which is seen to bear a resemblance to an adsorption isotherm.

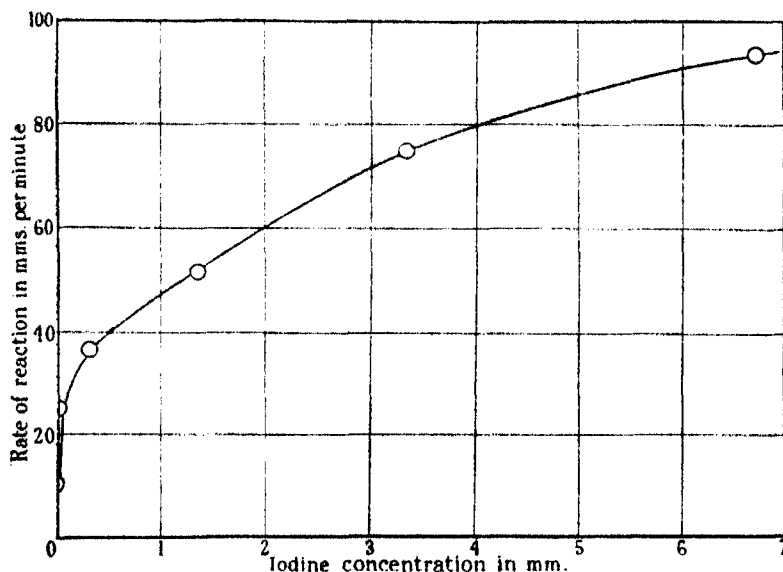


FIG. 2.—Acceleration of the Surface Reaction by Iodine.

Since the relative rates of the surface reaction and the gas reaction vary very much with conditions, the influence of iodine on the total reaction may change from a retardation to an acceleration in the same vessel as temperature and pressure are varied. The results given below refer to a porcelain bulb. At 560° C. with 200 mm. hydrogen and 100 mm. oxygen there is a very marked acceleration; at 580° C. with 300 mm. hydrogen and 150 mm. oxygen this has given place to a small but definite retardation, the inhibition of the gas

reaction more than compensating for the considerable acceleration of the surface reaction.

Porcelain Bulb.

	Amount of iodine as percentage of total pressure.	Time for 10 per cent. reaction.	Time for 20 per cent. reaction.
560° C. $H_2 = 200$ mm., $O_2 = 100$ mm.	0 0.167 0.55 1.11	' '' 9 55 1 55 1 25 1 10	' '' 22 15 4 25 3 0 2 10
580° C. $H_2 = 300$ mm., $O_2 = 150$ mm.	0 0.37	0 25 0 34	0 53 1 5

Similarly when the temperature in the sphere-packed bulb was increased the acceleration diminished considerably.

Sphere-packed Silica Bulb.

	Amount of iodine as percentage of total pressure.	Time for 25 per cent. reaction.	Time for 50 per cent. reaction.
600° C. $H_2 = 400$ mm., $O_2 = 200$ mm.	0 1.66 3.33	' '' 4 45 0 40 0 32	' '' 8 25 1 30 1 13
630° C. $H_2 = 400$ mm., $O_2 = 200$ mm.	0 1.85	0 17 0 16	0 45 0 37

The uninhibited gas reaction is retarded in a very marked way by a decrease in the dimensions of the reaction vessel, since the chains are broken at the wall. If the iodine inhibits the reaction by breaking chains in the gas, the rate of the retarded reaction should become much less dependent on the dimensions of the vessel. This anticipation was confirmed in a general way by experiments made in a set of three silica bulbs of different diameters. The simultaneous surface reaction complicates matters; but it is seen in the following table that all three bulbs give roughly the same rate with iodine:—

Temperature = 580° C. H_2 = 300 mm., O_2 = 150 mm.

Diameter of vessel (cm.).	Concentration of iodine (mm.).	Times required for 20, 40 and 80 mm. pressure change.		
		t_{20} .	t_{40} .	t_{80} .
3.2	0	' "	' "	' "
	1.66	1 55 0 50	4 5 1 41	11 54 4 11
4.9	0		Explosion	
	1.66	0 33	1 9	2 50
7.5	0		Explosion	
	1.66	0 43	1 26	3 39

Permanent changes in the bulb surface caused by exposure to iodine were observed, and greatly increased the difficulty of the experiments. The total rate of reaction drifts: for example, the time required for 20 per cent. reaction of a mixture of 200 mm. hydrogen and 100 mm. oxygen in an unpacked silica bulb at 540° C. decreased from 16 minutes 45 seconds to 1 minute 45 seconds in the course of about 20 experiments. In a packed bulb the rate drifted in the opposite direction. A possible change in the explosion pressure following exposure to iodine has already been referred to.

Comparison of Influence of Decomposition Products of Isopropyl Iodide with that of Iodine produced from Hydrogen Iodide.

In order to prove that the effects are due to iodine and not to the hydrocarbons from the isopropyl iodide, experiments were made with iodine produced by oxidation of hydrogen iodide in the reaction vessel; the hydrogen iodide was prepared by heating potassium iodide with syrupy phosphoric acid. The results, given below, show conclusively that the iodine alone is responsible.

(1) Upper Critical Explosion Limit.

Large unpacked silica bulb. Temperature = 507° C.		
Amount of iodine as percentage of total pressure.		Explosion pressure (mm. of mercury).
From isopropyl iodide.	From hydrogen iodide.	
0	0	60
0.0033	—	No explosion
—	0.0033	No explosion
0.00083	—	22
—	0.00083	31

(2) Surface Reaction.

Sphere-packed silica bulb. Temperature = 600° C. H_2 = 400 mm., O_2 = 200 mm.				
Amount of iodine as percentage of total pressure.		Times required for 10 per cent., 25 per cent. and 50 per cent. of complete reaction.		
From isopropyl iodide.	From hydrogen iodide.	t_{10} per cent.	t_{25} per cent.	t_{50} per cent.
0	0	' 6	' "	' "
0.167	—	0 28	1 10	20 40
—	0.167	0 30	1 10	2 55
				3 2

(3) High Pressure Gas Reaction.

Large unpacked silica bulb. Temperature = 550° C. H_2 = 200 mm., O_2 = 100 mm.				
Amount of iodine as percentage of total pressure.		Times required for 10 per cent., 25 per cent. and 50 per cent. of complete reaction.		
From isopropyl iodide.	From hydrogen iodide.	t_{10} per cent.	t_{25} per cent.	t_{50} per cent.
0	0	' "	' "	' "
0.5	—	0 48	1 30	2 40
—	—	1 17	3 15	7 46
0.5	0.5	1 25	3 37	8 35
0.0167	—	4 0	11 15	—
—	0.0167	4 17	11 37	—

Mechanism of the Action of Iodine.

At 550° C. the equilibrium $H_2 + I_2 = 2HI$ is rapidly established, but in presence of oxygen the equilibrium $4HI + O_2 = 2H_2O + 2I_2$ lies very far to the right. The existence of these two processes suggests at once a simple explanation of the mechanism by which the surface combination of hydrogen and oxygen is accelerated,* the effect being simply an example of "intermediate compound catalysis."

With regard to the inhibition of the explosion, since we have adopted the

* A similar catalysis may occur homogeneously; but its contribution to the total reaction must be more than counterbalanced by the simultaneous inhibition of the normal chain reaction.

working hypothesis that the upper limit is determined by deactivation in the gas, we must suppose that active molecules propagating the chains are deactivated by "collisions of the second kind" between, for example, H_2O_2 and I_2 ; or destroyed in a chemical reaction such as $\text{H}_2 \text{ active} + \text{I}_2 = 2\text{HI}$, or, in terms of Haber's theory, $\text{H} + \text{I}_2 = \text{HI} + \text{I}$. It is also conceivable that the iodine prevents the escape from the wall of something necessary for the starting of the chains.

The inhibition of the gas reaction at higher pressures may be due either to deactivation in the gas phase, as already indicated, or to an action of the iodine in increasing the chain-breaking efficiency of the walls. The fact, however, that the inhibited reaction tends to become independent of the dimensions of the vessel, in contrast with the uninhibited reaction, favours the first alternative, which we therefore adopt as our working hypothesis.

In the next section we simply consider a "deactivating" collision with iodine without assuming anything more about its nature. It is hardly necessary to point out that the pronounced inhibiting action which minute amounts of iodine can exercise provides further confirmation, if any is needed, of the chain-reaction character of the combination.

Efficiency of the Deactivating Collisions with Iodine.

In the region of high pressure and temperature, where the inhibiting action of iodine is exercised, the chains by which the uninhibited reaction is propagated end principally on the wall of the vessel. For an active molecule with the molecular weight of hydrogen peroxide the diffusion coefficient through 300 mm. hydrogen and 150 mm. oxygen at 550°C . is approximately 2.3, from the relation $D = 1/3 \bar{u}l$. The time taken for a chain to travel from the centre of the bulb of radius 3.75 cm. to the wall is found from the Einstein equation, $x^2 = 2Dt$, to be approximately 2.5 seconds. (For OH the value would be 1.8 seconds.)

From the formula

$$N\sigma_{12}^2\{8\pi RT(1/M_1 + 1/M_2)\}^{\frac{1}{2}}$$

we find, taking σ_{12} as 3.5×10^{-8} cm., that an active molecule of molecular weight 34, would make 3.5×10^6 collisions per second with iodine at 1 mm. pressure. From fig. 1 it appears that the pressure of iodine required to reduce the rate to one-half of its normal value is 1.63×10^{-3} mm. Thus at this pressure the total number of collisions with iodine made by an active molecule on the way to the wall is $3.5 \times 10^6 \times 1.63 \times 10^{-3} \times 2.5 = 1.4 \times 10^4$.

654 *Kinetics of Combination of Hydrogen and Oxygen.*

Now when the rate of reaction is reduced to one half, the chains must on the average be cut off at half their length. If normally they end on the wall and are never reflected, then when the rate is reduced to half there must have been on the average one effective collision with iodine on the way to the wall for each chain. The total number of collisions being 1.4×10^4 , the efficiency of a collision with iodine in breaking the chain must be 0.7×10^{-4} . If normally a chain is reflected backwards and forwards y times, then the efficiency is smaller still in this ratio.

This small efficiency does not suggest a mechanism of deactivation by an "elementary" reaction, in Polanyi's sense (where each collision is effective) unless that elementary reaction is highly endothermic.* At the present stage of knowledge it would be only guesswork to proceed further with theories about the details of a phenomenon, the general character of which, however, appears to be clear.

Summary.

The position of the investigation of the reaction between hydrogen and oxygen is summarised, and additional data are recorded about certain points previously studied.

The surface reaction in vessels of silica and porcelain is found to be accelerated by iodine.

The gas reaction occurring at relatively high temperatures and pressures is found to be retarded, and the explosion which normally occurs between certain limits of pressure to be inhibited. The amounts of iodine required are small. The efficiency of collisions with iodine in breaking chains is, however, found to be less than about 10^{-4} .

Water vapour is found to lower the upper critical limit of the low pressure explosion region, and, in sufficient amount, to inhibit the explosion altogether.

Commercial hydrogen appears to contain no inhibiting substances.

We are seeking to elucidate the mechanism of the inhibition further by studying the action of other halogens on this reaction, and also the inhibition of the oxidation of hydrocarbons.

We are greatly indebted to the Royal Society and to Imperial Chemical Industries, Ltd., for grants in aid of this work.

* There are examples, however, of elementary reactions with small efficiencies.

The Diffraction of Electrons in Mercury Vapour.

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Introduction.

Diffraction phenomena as exhibited in the experiments of Davisson and Germer, G. P. Thomson, Rupp, Kikuchi, and others have demonstrated in a very beautiful manner the wave nature of electrons. In these experiments the interference patterns found are due to a regular crystalline or molecular structure having a lattice spacing somewhat greater than the wave-length of the electrons employed.

In experiments on the scattering of slow electrons in monatomic gases we might expect to obtain an electrical analogue of the optical case when light passes through a cloud of minute water drops producing diffraction halos such as those seen around the sun or the moon, for the classical diameter of the scattering atoms will be only slightly greater than the wave-length of the electrons.

Bullard and Massey in a paper now in course of publication have recently examined the scattering in argon of electrons of from 4 to 40 volts energy over an angular range of from 15° to 125° . They have obtained angular scattering curves showing one or two well-marked maxima and minima which are somewhat similar to those representing the diffraction of light by a random distribution of small scattering spheres.

Previous work* on the angular scattering of electrons in gases has been confined to somewhat higher voltages and considerably smaller scattering angles (not exceeding 60°). The results show only a steady decrease in the intensity of the scattered current with increase of the scattering angle.

The present paper deals with the angular scattering of electrons in mercury vapour over an angular range of from 18° to 126° . Results are shown for 15 different velocities of the primary beam between 8 and 800 volts. All the curves show distinct maxima and minima, maxima of four different orders being obtained.

* Dymond and Watson, 'Proc. Roy. Soc.,' A, vol. 122, p. 571 (1929); Harnwell, 'Phys. Rev.,' vol. 34, p. 661 (1929); Arnot, 'Proc. Roy. Soc.,' A, vol. 125, p. 660 (1929); Green, 'Phys. Rev.,' vol. 36, p. 239 (1930); McMillen, 'Phys. Rev.,' vol. 36, p. 1034 (1930).

Apparatus.

The apparatus used for this work has been fully described elsewhere,* and the reader is referred to this paper for a detailed account of it. It will be sufficient to give here a diagram of the essential parts, fig. 1. These are an electron gun consisting of the tungsten filament, *F*, entirely enclosed within two cylinders containing two holes, *S*₁ and *S*₂, each 1 mm. in diameter. The gun could be rotated about the axis *O* through nearly 360° by means of a small ground glass joint. The gun produced a sharp electron beam of about 1 mm. in cross section which did not appreciably diverge. The reason for this has been shown by the author in the paper mentioned above to be due to a radial potential gradient around the beam which holds it together.

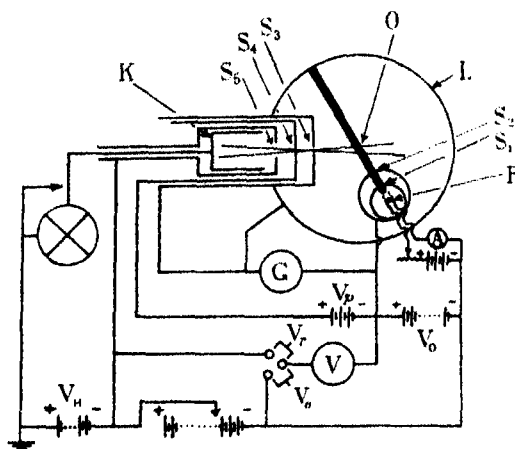


FIG. 1. —Diagram of Apparatus.

The receiving system consisted of three concentric cylinders containing the slits *S*₃, *S*₄, *S*₅, and the concentric Faraday cylinder, *K*, within the inner shielding cylinder. The dimensions of these slits were respectively 8 mm. × 0.2 mm., 5 mm. × 0.2 mm., 2 mm. × 2 mm., and the three slits were equally spaced 5 mm. apart. The distance of *S*₃ from the scattering point, *O*, was 12 mm. The inside of the collision chamber was lined with the large nickel cylinder, *L*.

A small difference of potential, *V*_p, of about 6 volts was applied to the first two slits, *S*₃ and *S*₄, to stop positive ions from entering the Faraday cylinder. A potential of *V*_r = (*V*₀ + *V*_p - 3) volts, where *V*₀ is the velocity of the primary electron beam, was applied between the next two slits, *S*₄ and *S*₅, so

* Arnot, 'Proc. Roy. Soc.,' A, vol. 129, p. 361 (1930).

as to stop all but the elastically scattered electrons from being received. And finally a potential, V_H , of 21 volts was applied between the slit S_5 and the Faraday cylinder to prevent any secondary emission of electrons from the Faraday cylinder. The current in the electron beam was measured directly by the galvanometer, G. Beams of from 0.3 to 15 microamps were employed.

The glass work was of pyrex, and the whole apparatus up to within a few centimetres of the ground glass joints was baked out at a temperature of 500° C., the joints being kept below room temperature by means of water coolers.

The apparatus was connected through a liquid air trap to a diffusion pump backed by a Hyvac pump, and a good "sticking" vacuum was obtained on a sensitive McLeod gauge. The apparatus was quite vacuum-tight, showing a rise in pressure of less than 2×10^{-4} mm. when left cut-off for 24 hours. During a run the pumps were kept going with no liquid air on the trap, which contained a little mercury at the bottom. The pressure of mercury vapour inside the apparatus was consequently that corresponding to room temperature, i.e., about 10^{-3} mm. of Hg. The mean free path of an electron at this pressure is about 30 cm., so that the probability of an electron making two collisions before entering the Faraday cylinder was very small.

Retarding potential curves, although not quite as sharp, were similar to those obtained by the author with an earlier form of apparatus.* The group representing the electrons which had been scattered elastically showed that the homogeneity of the primary beam was good, 86 per cent. of the electrons having a velocity within less than 2 volts of the mean.

The author† has recently made a detailed investigation of the passage of an electron beam through a field-free enclosure, and has shown that a small radial potential gradient is set up around the electron beam. It has been shown‡ that the effect of this gradient on electron scattering experiments is to introduce a small error into the angle of scattering. In the experiments described in the present paper this error is always less than the experimental error made in measuring the angle (about 1°).

Results.

(1) *Blank Tests in vacuo.*—Liquid air was put on the mercury vapour trap, and the apparatus was baked out for 3 or 4 hours at 500° C. Several runs were then taken *in vacuo* at various different values of V_0 , the potential applied to

* 'Proc. Roy. Soc.,' A, vol. 125, p. 660 (1929).

† 'Proc. Roy. Soc.,' A, vol. 129, p. 361 (1930).

‡ 'Proc. Camb. Phil. Soc.,' vol. 27, p. 73 (1931).

the primary electrons. For all values of V_0 , with the exception of a run at $V_0 = 8.6$ volts, the current at all angles between 5° and 125° was never more than a few per cent. of the scattered electron current obtained when mercury vapour at 10^{-3} mm. was present in the apparatus. When V_0 was 8.6 volts the current *in vacuo* was about 30 per cent. of the scattered current in mercury vapour, between 75° and 125° , though for smaller angles it was very much less. For all values of V_0 the current *in vacuo* between 60° and 125° was constant. In no curves taken *in vacuo* was there any trace of maxima or minima.

(2) *Angular Scattering in Mercury Vapour.*—During each reading of the electrometer the strength of the electron beam as recorded by the galvanometer (G, fig. 1) was noted. The electrometer readings were then divided by the galvanometer readings so as to correct for any variation in the intensity of the beam. Generally this variation was not more than a few per cent. Readings were taken on both sides of the electron beam and the true angular zero was determined from the symmetry of the resulting curve. Fig. 2 shows

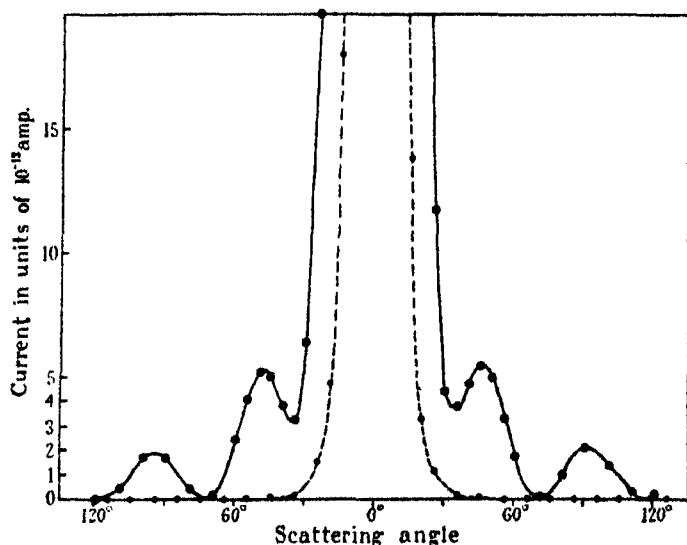


FIG. 2.—Angular Distribution of 379 volt Electrons (without $\sin \theta$ correction).
Broken curve is a run *in vacuo*.

a typical result for 379 volt electrons. The broken curve is a run taken *in vacuo* with the same intensity and velocity of the electron beam. To obtain the true variation of the intensity of scattered current with angle, θ , the ordinates

* Corresponding to a temperature of 18° C. Obtained from the "International Critical Tables," vol. 3, p. 206.

Table I.—Intensity of Scattered Current in units of 10^{-13} amps.

Velocity of primary electrons in volts.

Angle.	8.6.	14.	19.	23.	30.	41.	46.	54.	82.	119.	207.	379.	480.	610.	800.
°															
18	—	—	—	—	—	—	—	—	120	—	—	30.8	22.4	19.0	15.4
24	—	—	—	—	—	—	—	—	70.0	—	30.8	9.80	9.80	6.10	8.11
30	252	56.0	33.6	25.2	30.5	25.7	43.4	24.4	41.5	25.5	9.80	2.38	3.66	3.73	3.69
36	168	27.1	8.96	5.31	11.2	13.2	27.7	17.9	23.0	11.2	1.96	2.18	2.66	3.08	2.49
42	119	15.1	4.60	5.31	8.40	10.7	14.2	13.8	13.3	5.30	1.88	3.22	2.96	2.55	1.59
48	86.8	8.40	4.85	7.56	11.4	11.9	13.8	10.8	7.63	3.64	3.50	3.97	2.69	1.96	1.01
54	64.3	6.16	6.30	9.45	13.0	11.6	10.4	8.04	4.25	3.27	5.31	3.22	1.82	0.84	0.50
60	47.6	5.89	6.38	8.90	11.7	9.94	7.70	5.96	2.91	3.84	4.81	1.68	0.64	0.48	0.28
66	36.4	5.63	5.31	7.20	8.86	7.22	5.19	4.17	2.44	4.25	3.27	0.39	0.22	0.08	0.36
72	30.8	5.38	4.06	5.03	5.73	4.20	3.08	2.71	2.38	4.40	1.48	0.08	0.34	0.59	0.59
78	27.4	4.99	2.80	3.08	2.80	1.74	1.40	1.87	2.89	4.09	0.28	0.56	0.78	1.15	0.67
84	24.6	4.62	2.24	2.57	1.48	0.90	1.32	1.87	3.27	3.25	0.17	1.68	1.46	1.29	0.62
90	22.6	4.74	2.44	2.71	1.90	1.06	2.89	2.52	3.30	2.26	0.17	2.01	1.68	0.98	0.34
96	21.5	5.03	3.08	3.05	3.56	3.84	5.23	4.06	3.22	1.62	0.20	1.85	1.40	0.39	0.08
102	20.7	5.40	3.64	3.50	5.12	6.09	6.79	5.42	3.00	1.01	0.25	1.18	0.90	0.08	0.03
108	21.8	5.51	3.41	3.64	6.09	7.99	5.94	6.37	2.62	0.48	0.31	0.45	0.50	0.11	0.20
114	24.9	5.15	2.74	3.11	5.58	8.40	2.80	6.16	1.90	0.25	0.36	0.25	0.42	0.56	0.56
120	28.0	4.95	1.90	2.41	4.06	7.00	0.90	4.84	1.26	0.25	0.48	0.20	0.67	1.06	0.87
126	30.0	4.81	1.46	1.68	2.29	—	0.62	3.34	0.56	—	0.56	—	1.12	1.48	0.92

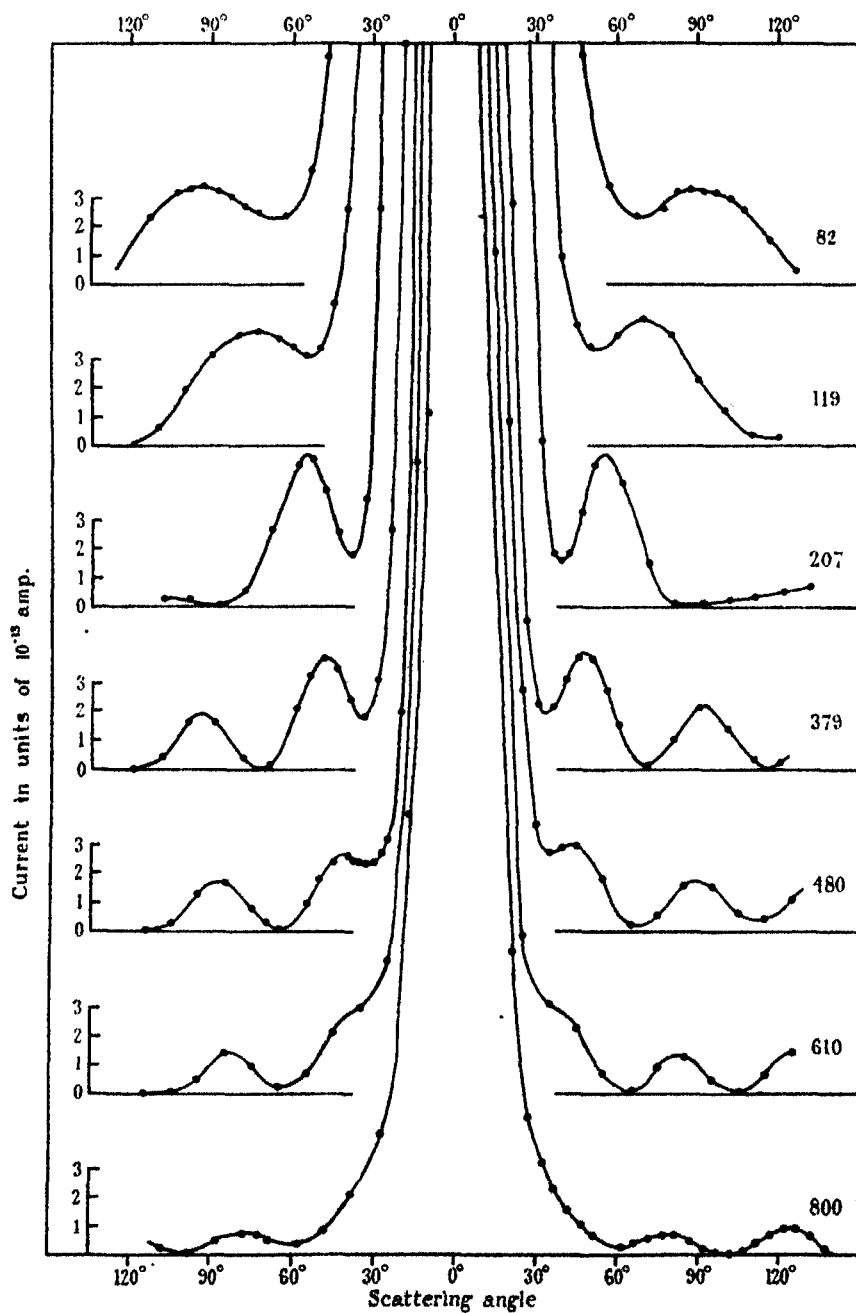


FIG. 3.—Angular Distribution of Scattered Electrons. Curves for 800, 610, 480, 379, 207, 119 and 82 volt Electrons.

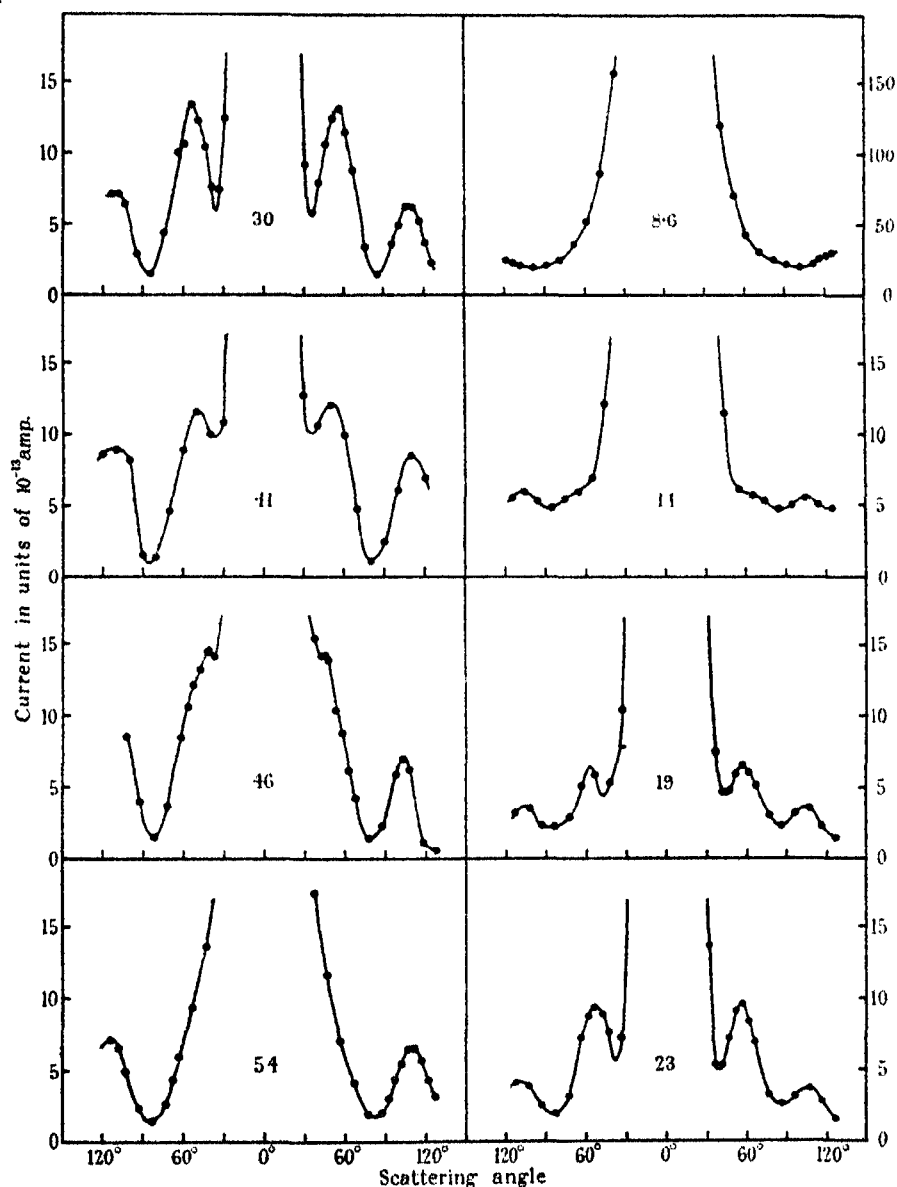


FIG. 4.—Angular Distribution of Scattered Electrons. Curves for 54, 46, 41, 30, 23, 19, 14 and 8.6 volt Electrons.

of fig. 2 must be multiplied by $\sin \theta$ in order to take into account the change in the scattering volume with angle. This may be readily seen from fig. 1, for the effective length of path for collision is the length of the electron beam intercepted by the beam entering the Faraday cylinder which is defined by the slits

S_3 and S_4 . If d is the width of this beam where it intersects the electron beam, then the effective length of path for collision is $d/\sin \theta$. The value of d is 1.16 mm.

The results for 15 different velocities of the electron beam, from 8.6 to 800 volts, are shown in figs. 3 and 4. All these curves have been corrected for the above mentioned change of scattering volume with angle. They have all been reduced to a standard pressure of 10^{-8} mm. of Hg,[†] and a standard electron beam current of 7.4 microamps. The ordinates represent the current received by the Faraday cylinder in units of 10^{-13} amps. Table I gives the ordinates in these units at intervals of 6° from 18° to 126° . In comparing these curves it should be noticed that fig. 4 has been reduced to half the scale of fig. 3, and that the ordinates of the 8.6 volt curve in fig. 4 have been still further reduced by factor of 10.

Fig. 5 shows the small angle scattering of 82 volt electrons. The ordinates of this figure are also in units of 10^{-13} amps. The points represented by dots

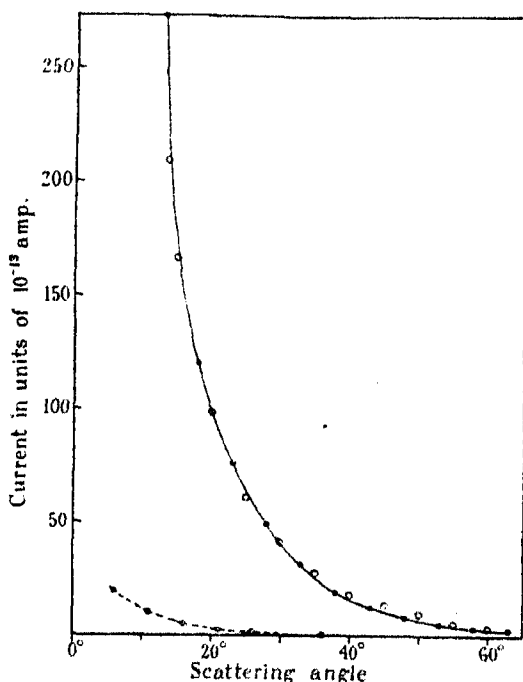


FIG. 5.—Angular Distribution of 82-volt Electrons. Broken curve is a run *in vacuo*.

are those obtained with the present apparatus; those represented by circles are taken from a curve which was obtained with an earlier type of apparatus,

and which has already been published.* The circles have been fitted to the curve through the dots at 30° . The broken curve is a run taken *in vacuo* with the same intensity and velocity of the electron beam. In this earlier work attention was mainly confined to the small angle scattering (5° to 55°) and results up to 55° only were published. Two runs were, however, taken at larger angles, and in both these curves there is evidence of a slight hump with a maximum at about 90° . The height of this hump was just about the size of the experimental error, and owing to trouble being experienced with the oxide coated filament used in the earlier apparatus it was not possible to increase the intensity of the scattered current at 90° sufficiently to determine if the hump was genuine. Moreover, as the maximum of this hump appeared at 90° it was thought that, if genuine, it might be connected in some way with the strong positive drift noticed at large angles which also reached a maximum at 90° , and it was consequently left until this positive drift was further investigated. This has since been done, and the drift shown (*loc. cit.*) to be due to positive ions accelerated out of the electron beam at right angles to it by a radial potential gradient set up around the beam by space charge. In the present apparatus provision was made for stopping these positive ions by inserting an extra slit in the receiving system.

The Absolute Scattering.

In trying to determine the absolute scattering, *i.e.*, the number of electrons scattered through an angle, θ , per unit solid angle from a primary beam of known intensity after travelling unit distance through a gas at a given pressure, one is faced with the difficulty that the effective area of a slit for slow electrons is not necessarily its geometrical area. However, an estimate of the absolute scattering which is probably correct to within 50 per cent. can be made by taking the effective area of a slit to be equal to its geometrical area. Another difficulty is encountered in determining the solid angle in which electrons are collected by the Faraday cylinder. If the angle between the two extreme rays entering the Faraday cylinder in a vertical plane be $d\theta$, and in a horizontal plane be $d\phi$, then the Faraday cylinder receives electrons scattered in a solid angle $d\theta d\phi$. The angle $d\theta$ is defined by the width of the slits S_3 and S_4 and is about 4.6° . The angle $d\phi$ is defined by the slit S_5 and the width of the electron beam which cannot be determined accurately. If the width of the electron beam is taken as 1 mm., $d\phi$ is equal to 7.8° , and therefore the solid

* Arnot, 'Proc. Roy. Soc.,' A, vol. 125, p. 660 (1929).

angle in which electrons are received by the Faraday cylinder is 8.7×10^{-4} of the total solid angle around a point. We now have the following data for all graphs in this paper :—

Unit ordinate of graph	$= 10^{-13}$ amp.
Electron beam current	$= 7.4 \times 10^{-6}$ amp.
Solid angle for collection of electrons.....	$= 8.7 \times 10^{-4}$.
Length of path for collision	$= 0.116$ cm.
Pressure	$= 0.001$ mm. of Hg.

Therefore the number of elastically scattered electrons per unit primary electron, per unit solid angle, per centimetre path, per unit ordinate of graph, at a pressure of 0.001 mm. of Hg is equal to 1.34×10^{-4} . Thus an estimate of the absolute scattering can be found from Table I by multiplying by this factor. In Table II the absolute scattering of 82 volt electrons determined by the present apparatus and calculated from fig. 5 is compared with the values obtained by the earlier apparatus, and which have been calculated from data given in my former paper.* It will be seen that the agreement is very satisfactory.

Table II.—Single scattering of 82 volt electrons in mercury vapour. $I_1(\theta)$ is the number of electrons elastically scattered through an angle, θ , per unit solid angle, per primary electron, per centimetre path, at a pressure of 0.001 mm. of Hg. $I_2(\theta)$ is the corresponding quantity obtained with the earlier form of apparatus.

θ .	$I_1(\theta)$.	$I_2(\theta)$.
0	—	—
5	—	0.125
10	—	0.0515
15	0.0237	0.0242
20	0.0132	0.0144
25	0.0084	0.0088
30	0.0055	0.0060
35	0.0035	0.0041
40	0.0021	0.0027
45	0.0014	0.0019
50	0.00086	0.0014
55	0.00054	0.00075
60	0.00039	0.00050

* *Loc. cit.* These values were originally calculated by Compton and Langmuir from the scattering curve given in my paper (see 'Revs. Mod. Phys.,' vol. 2, p. 233). I have recalculated the values, using the original curves, and have added values for three more angles.

Discussion.

It is seen from figs. 3 and 4 that all the scattering curves show well marked maxima and minima. As the velocity of the primary electron beam is increased the peaks in general move in to smaller angles until finally they can no longer be resolved owing to the rapid increase of scattering at very small angles. The two distinct maxima in the curve for 19-volt electrons both eventually become lost in the main peak at 0° , the first between 46 and 54 volts, and the second between 610 and 800 volts.

If we treat the scattering gas as a random distribution of small rigid spheres, then by analogy with the optical case we should expect the diffraction maxima to move in to smaller angles as the wave-length of the incident waves is decreased, *e.g.*, as the velocity of the incident electrons is increased. If the effective diameter of the scattering atoms is also a function of the velocity of the incident electrons, then the direction of movement of the diffraction maxima will depend upon that function. Blackett* has shown from a consideration of dimensions that this function depends upon the law of force in the atom. For an inverse square law of force the effective diameter of the atom varies inversely as the square of the velocity, and consequently the diffraction maxima in this case would move out to larger angles as the velocity of the incident electrons was increased. If, however, the atomic forces vary inversely as a high power of the distance, such as is the case in the outer regions of the mercury atom, then the effective diameter of the atom is approximately independent of the velocity, and we should therefore expect the diffraction maxima to move in to smaller angles with increasing velocity of the incident electrons, as is found to be the case.

The angular position of the maxima are given in Table III, where for the purpose of comparison the inner peak in the 19 volt curve has been taken as the first order maximum.

It will be noticed that on increasing the velocity of the incident electrons the second order maximum at first moves in to smaller angles. At $V_0 = 19$ volts it begins to move out to larger angles until $V_0 = 46$ volts, when it again changes direction and moves in steadily until it becomes lost in the main peak at 0° . This change of direction of movement between 19 and 46 volts is probably due to a hump in the cross section curves for mercury vapour which occurs in the region of this velocity.† This effect will be discussed shortly in a letter to 'Nature.'

* Blackett, 'Proc. Camb. Phil. Soc.,' vol. 23, p. 698 (1927).

† See Brode, 'Proc. Roy. Soc.,' A, vol. 125, p. 134 (1929).

Besides the position, the relative intensity of the peaks is of considerable interest. The fourth order maximum which appears in the 610 volt and the 800 volt curves appears to be slightly higher than the third order maximum in these two curves.

Table III.—Angular Position of the Maxima in the Scattering Curves.

Order.	Velocity of primary electrons in volts.													
	14.	19.	23.	30.	41.	46.	54.	82.	119.	207.	379.	480.	610.	800.
1	—	56	55	54	50	(43)	—	—	—	—	—	—	—	—
2	108	105	106	110	112	113	111	90	72	55	48	(44)	—	—
3	—	—	—	—	—	—	—	—	—	—	93	89	83	78
4	—	—	—	—	—	—	—	—	—	—	—	—	—	125

As the velocity of the primary beam is decreased from 800 volts the intensity of the peaks in general increases until V_0 is about 30 or 40 volts, after which the peaks appear to decrease in height and become less sharply marked. In the 14 volt curve the peaks are just perceptible, and appear to be superimposed upon a large background of almost uniform scattering. The relatively large scattering at large angles observed in the 8·6 volt curve is probably due to the rapid increase in the cross section of the atom for electrons of about this velocity.*

Born† has developed an approximate theory of the scattering of electrons by atoms. This theory does not take into account the distortion of the incident wave by the atomic field, and cannot therefore be applied to the scattering of slow electrons, since for slow electrons the wave-length, which varies with the reciprocal of the velocity, will be considerably altered by the field of the atom. By taking this change of wave-length into account Holtsmark‡ has successfully accounted for the Ramsauer effect in argon and krypton; but Oppenheimer§ has pointed out that an exact solution of the problem must also include the effect of interchange between the atomic and impacting electrons. The results described in this paper should provide a definite test

* See Brode, 'Proc. Roy. Soc.,' A, vol. 125, p. 134 (1929).

† 'Z. Physik,' vol. 38, p. 803 (1926).

‡ 'Z. Physik,' vol. 55, p. 437 (1929); *ibid.*, vol. 66, p. 49 (1930).

§ 'Phys. Rev.,' vol. 32, p. 361 (1928).

of the complete wave theory treatment of collisions when the distortion of the incident wave by the atomic field, the effect of polarisation of the atom by the incident electron, and the interchange effects can all be taken into account.

Summary.

An investigation of the angular scattering of electrons in mercury vapour over an angular range of from 18° to 126° is described. Results are shown for fifteen different velocities of the primary beam between 8 and 800 volts. All the scattering curves show distinct maxima and minima, maxima of four different orders being obtained. An estimate of the absolute scattering is given.

The absolute scattering of 82 volt electrons between 15° and 60° has been re-determined, and the results are in good agreement with the author's earlier work between this range. The work is at present being continued with other gases.

In conclusion, I wish to express my thanks to Lord Rutherford and Mr. P. M. S. Blackett for their interest and advice in this work, and to Mr. C. B. Mohr for his assistance in taking some of the readings. I am also indebted to Trinity College for a research grant from the Rouse Ball Fund.

*On the Variability of the Quiet-Day Diurnal Magnetic Variation.
Part II.*

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Introduction.

1. This paper is a sequel to our former one* relating to the daily magnetic variation, on really quiet days, at Eskdalemuir and Greenwich. Here we extend the investigation to four more magnetic observatories; the principal relevant particulars for the whole six observatories are as follows:—

Table I.

Observatory.	Abbreviation.	Geographical latitude.	Longitude.	Magnetic latitude.	H.	Z.	Dec.
		°	°	°			°
Eskdalemuir	E	55·3 N	3·2 W	58·5 N	16700	45100	17 W
Greenwich	G	51·5 N	0·0	54·0 N	18400	43200	14 W
Ebro	Eb	40·8 N	0·5 E	43·9 N	23300	36800	12 W
San Fernando.....	SF	36·5 N	6·2 W	41·0 N	25000	34000	14 W
Batavia	B	6·2 S	106·8 E	18·0 S	36700	—22600	1 E
Mauritius	M	20·1 S	57·6 E	26·6 S	23100	—30300	10 W

The last three columns give approximate mean values of the three magnetic elements, H (horizontal force), Z (downward vertical force) and declination.

The stations range over 75° of geographical latitude, and 85° of magnetic latitude (*i.e.*, latitude with respect to the earth's magnetic axis).

1.1. Fuller knowledge and understanding of the daily magnetic variations on quiet days is obtainable along three main avenues; one is the detailed study and intercomparison of the data directly afforded by the various observatories; another is their representation and discussion in mathematical terms, particularly by means of spherical harmonic functions; the third is by hypothetical enquiry into their physical causes. All three methods are useful and necessary, but the first two must precede the third. The second method is indispensable in certain directions, but it has the disadvantage that nature will not readily

* "On the Variability of the Quiet-day Diurnal Magnetic Variation at Eskdalemuir and Greenwich," 'Proc. Roy. Soc.,' A, vol. 123, p. 27 (1929).

be fitted to the procrustean bed of our mathematical formulæ, and to render the analysis practicable, some features of the phenomena have to be ignored or averaged out. For some purposes, therefore, the first method is the only suitable one, despite the enormous labour of computation involved in it—a labour little to be suspected, by one unacquainted with geophysical investigations, from the appearance of the results finally presented. This is the method here followed. The main, though not sole, object of the enquiry has been to determine whether the day-to-day variability of the daily magnetic variation is a local or a world-wide phenomenon.

1.2. The former paper showed that there was considerable, though not complete, parallelism between the day-to-day variations at Eskdalemuir and Greenwich, which are only a few degrees apart. The present paper examines the same question for observatories over a wide range of latitude, but chosen to be as near together in longitude as the distribution of magnetic observatories will permit. To obtain southern stations it was necessary to depart rather far from the Greenwich meridian. In a later paper it is intended to examine the question expressly for observatories well spaced in longitude.

1.3. The present limitation in longitude was imposed because the days to which the investigation primarily refers are *Greenwich days*; they are chosen as having international character figures 0·0 or 0·1 (denoting extreme magnetic quiet), and these figures relate to the Greenwich day.

1.4. In a later paper we hope to present an extension of the results given in our former paper (§§ 19–21) on the relation between the daily range on very quiet days, and the non-cyclic variation and the departure of the daily mean from the monthly mean.

Description of the Original Data.

2. In the period 1913–1923 covered by our work, the following were the elements for which the various observatories gave published data :—

E	G	Eb	SF	B	M
N, W, V	N*, D, V	H, D, V	H, D	N, E, V	H, D, V

* Except that H was recorded instead of N in 1913, 1914.

Here N, W, E denote north, west or east force respectively, D the westerly declination (in angular measure) and V the vertical force, positive downwards at E, G and Eb, and upwards at B and M.

All D data have been converted into force units, but H and D (force) data have not been transformed into N and W. In some of the tables, however, they are referred to as N and W (from which, at the stations considered, they do not differ much) in order to avoid having multiple headings for rows and columns. Actually, however, N denotes H at Eb, SF and M, while W denotes D except at E and B; the east force at B has been reversed to obtain W. The choice of N and W for this purpose of notation is to indicate, at sight, at least the *approximate* direction to which the force refers.

2.1. Except for occasional days of lost record, each of the six observatories provides data for the whole period 1913–1923, save in the case of M, for which no data for 1913 and 1914 are published. No V data, however, are available at SF.

At E the published hourly values are means centred at exact hours of Greenwich mean time (G.M.T.). At G during 1913 and 1914 small irregularities in the magnetograms were first smoothed out, and then instantaneous values were read off; from 1915 onwards, the hourly values are means for the intervals between successive exact hours of G.M.T. At Eb, SF, M and (to the end of 1919) at B, instantaneous values for the hours of *local* mean time are published; from 1920 the B values are hourly means centred at the half-hours of standard mean time, 7 hours in advance of G.M.T. Fortunately the distinction between hourly values and hourly means is unimportant on the very quiet days here considered.

2.2. The data discussed in this paper consist of the daily ranges R, in force units (1γ); that is, the range in the 24 published hourly values for each day; on quiet days this will be nearly identical with (but slightly less than) the actual range between the extremes for the day.

The local day at M is 4 hours in advance of the Greenwich day, and therefore R in any element at M is not exactly comparable with that for a station on the Greenwich meridian; however, the maxima and minima in all three elements at M, on quiet days, usually fall within the period common to the Greenwich day and the local day at M.

At B the local time is 7 hours in advance of Greenwich, but here also, in W, the extreme values on quiet days usually fall in the period common to the G and B days, the times being roughly 3h. and 9h. G.M.T. (or 10h. and 16h. B.M.T.). In N the time of maximum is about 4h. G.M.T. or 11h. B.M.T., but the minimum falls about equally often near 9h. G.M.T. (16h. B.M.T.) or –6h. G.M.T. (1h. B.M.T.). In V the minimum occurs at about 6h. G.M.T. or 13h. B.M.T., but the maxima occur round about either 0h. or 12h. or 24h.

G.M.T. In all cases, however, for N, W and V, the value of R has been taken from the Batavia local day, overlapping the Greenwich quiet day for 17 hours, but including a previous 7 hours not in the Greenwich day.

The Quiet Days.

3. The quiet days used here, as in our former paper, include all those of international character figure 0·0 or 0·1, in the well-developed sunspot cycle 1913–1923. The number of days of each kind per year (all months) or month (all years) is given in Tables I, II of our earlier paper. A remarkable circumstance regarding these days (819 in all), which was not there noted, is that less than a third of them are isolated—the others fall in groups of two or more consecutive days. The distribution of the days in each year, in this respect, is indicated in Table II. The distribution is given also for all years, and for the two groups of years of greater and less sunspottedness formerly considered by us, and denoted by the symbols $\square$ and $\sqcup$; these years are, for $\square$, 1915–1919 (5 years, mean sunspot number 70·5), and for $\sqcup$, 1913, 1914, 1920–1923 (6 years, mean sunspot number 15·8). When a group of consecutive days overlapped from one year to the next, all the days in it were for the purpose of this table reckoned as belonging to the former year; this occurred in 1917–1918, where a pair overlapped from one to the other; hence the total for 1917 includes one day more, and for 1918 one day less, than in the Table I already quoted. Likewise 1913, January 1, was a member of a pair beginning in 1912, outside the period covered in this investigation; hence this day was omitted in forming Table II, which consequently refers to 818 instead of 819 days.

Table II.—Distribution of Sequences of Selected Quiet Days.

Year:	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	$\square$	$\sqcup$	All
All 0·0 and 0·1 days:	95	97	92	59	66	59	56	76	61	60	98	332	486	818
Number of isolated days	30	19	27	22	29	15	25	23	27	16	18	118	133	251
Sequences of 2 days	14	16	13	6	10	8	14	13	6	10	17	51	76	127
“ 3 “	8	7	3	7	3	5	1	3	6	4	10	19	38	57
“ 4 “	3	2	4	1	1	3	—	2	1	1	4	9	13	22
“ 5 “	—	1	—	—	1	—	—	2	—	—	—	1	3	4
“ 6 “	—	2	1	—	—	—	—	—	—	—	—	1	2	3
“ 7 “	—	—	—	—	—	—	—	—	—	—	—	0	0	0
“ 8 “	—	—	1	—	—	—	—	—	—	1	—	1	1	2
Number of possible pairs	39	50	43	23	23	27	16	33	21	28	49	132	220	352

It will be seen from this table that there are actually two sequences of 8 consecutive very quiet days, three of 6 days, and four of 5. The sets of 8 days were 1915, July 14 to 21, and 1922, December 16 to 23; and of 6 days, 1914, April 29 to May 4; 1914, November 20 to 25; and 1915, June 1 to 6.

The percentages of days falling in sequences of 1, 2, 3, ... 8 days were as follows :—

Table III.

Number of days in sequence :	1	2	3	4	5	6	7	8
Percentage of days—								
□	36	31	17	11	2	2	0	2
□	27	31	23	11	3	2	0	2
All years	31	31	21	11	2	2	0	2

The number of very quiet days per year in □ years is slightly less than that in □ years, but there is no great difference between them as regards distribution in sequences, though long series are naturally somewhat less common near sunspot maximum.

In the last row of Table II the number of possible pairs of consecutive quiet days available in each year (as required for later work—cf. § 10) is indicated. The distribution of the possible pairs according to months was as follows: the letters ns, e, w denote, as in our former paper, (northern) summer, equinox, and winter, or May to August; March, April, September, October; and November to February.

Table IV.

J	F	M	A	M	J	J	A	S	O	N	D	ns	e	w
25	28	22	30	34	32	41	19	22	28	40	41	126	102	124

This table shows no marked annual variation in the aggregation of quiet days into sequences.

The average length of a sequence (including each of the 251 isolated days as sequences) is 1.75 day (all years), or 1.66 day in □ years, 1.83 day in □ years.

Examination of the days immediately preceding or succeeding the 251 isolated quiet days showed that 109 (or 43 per cent.) had an adjacent day of character 0.2, and a further 58 (or 22 per cent.) had one of character 0.3. Thus if the definition of a pair of quiet days were extended to include "0.2"

days, only 142 (or 17 per cent.) of our 818 days would be isolated, and only 94 (or 10 per cent.) if "0.3" days also were included.

The Mean Ranges $\bar{R}$.

4. The first stage of the work consisted as before in the determination of the mean ranges $\bar{R}$ for each year (all months), given in Table V, and for each month (all years), given in Table VI. In forming these means, the mean

Table V.—Mean Range for each Year (all months). Unit 1 γ .

Year :	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	Δ	∇	All
Sunspot numbers :	1.4	9.6	47.4	57.1	103.9	80.6	63.6	37.6	26.1	14.2	5.8	70.5	15.8	40.7
$\bar{R}$ (Eb N)	24.5	23.5	29.4	32.4	32.9	28.1	28.1	28.1	24.2	23.9	21.4	30.2	24.3	27.0
$\bar{R}$ (Eb W)	44.2	43.2	54.0	61.0	67.9	56.2	54.7	52.5	48.3	39.6	41.0	58.8	44.8	51.1
$\bar{R}$ (Eb V)	22.0	21.0	22.4	29.3	41.3	30.8	27.5	28.9	34.8	20.8	22.0	30.3	23.3	26.4
$\bar{R}$ (SF N)	25.5	26.5	31.8	29.5	37.2	32.9	31.7	31.4	28.2	27.6	26.7	32.6	27.6	29.9
$\bar{R}$ (SF W)	42.8	41.7	51.6	52.8	66.9	56.4	46.8	53.7	46.8	36.8	39.6	54.9	43.6	48.7
$\bar{R}$ (B N)	38.4	40.1	50.9	49.1	59.7	57.9	56.7	48.2	45.2	39.8	39.2	54.9	41.8	47.7
$\bar{R}$ (B W)	36.5	36.6	44.5	43.4	50.4	47.8	48.7	40.9	44.3	38.9	34.9	47.0	38.7	42.4
$\bar{R}$ (B V)	25.1	25.6	32.1	33.0	43.7	37.2	38.0	30.8	27.7	27.1	23.4	36.8	26.6	31.2
$\bar{R}$ (MN)	—	—	28.1	27.3	32.2	27.9	29.3	28.6	26.7	24.8	22.0	29.0	25.5	27.4
$\bar{R}$ (MW)	—	—	44.2	46.1	58.1	59.2	52.7	45.6	44.2	42.7	37.6	52.1	42.5	47.8
$\bar{R}$ (MV)	—	—	21.2	23.5	23.7	21.1	19.8	20.8	21.8	19.3	20.3	21.9	20.5	21.3

Table VI.—Mean Range for each Month (all years). Unit 1 γ .

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
$\bar{R}$ (Eb N)	24.6	22.7	21.6	25.9	29.7	30.0	35.0	39.6	33.9	24.2	19.8	20.8
$\bar{R}$ (Eb W)	32.3	36.0	53.5	65.2	60.4	65.0	65.0	61.5	59.8	54.1	37.6	26.7
$\bar{R}$ (Eb V)	16.4	21.0	30.9	35.5	33.0	33.4	31.1	27.7	25.4	28.9	19.9	14.5
$\bar{R}$ (SF N)	28.1	28.1	28.3	28.9	36.7	32.1	37.9	36.7	33.9	23.2	23.0	23.3
$\bar{R}$ (SF W)	35.6	36.3	49.8	60.1	56.0	58.5	60.6	59.1	55.2	49.3	39.0	30.8
$\bar{R}$ (B N)	45.7	48.4	53.3	53.9	45.7	42.4	45.4	50.3	53.3	51.9	41.1	41.4
$\bar{R}$ (B W)	54.3	55.9	41.9	35.9	31.2	26.7	31.3	40.4	44.8	51.7	48.2	47.1
$\bar{R}$ (B V)	26.2	37.9	36.6	35.0	25.0	23.5	21.5	24.7	32.1	41.0	32.2	30.0
$\bar{R}$ (MN)	28.1	28.6	29.9	29.1	22.7	25.6	26.1	26.7	23.4	26.9	31.0	29.3
$\bar{R}$ (MW)	49.0	58.3	55.4	49.4	38.8	31.2	38.8	44.9	52.8	54.5	51.0	46.3
$\bar{R}$ (MV)	19.3	22.3	25.1	23.0	18.7	17.2	21.1	23.0	26.1	22.0	17.6	18.9

range for each month in each year was given equal weight, however many or few quiet days it included; no distinction was made between 0.0 and 0.1 days. The results are illustrated in figs. 1 and 2, which also include the

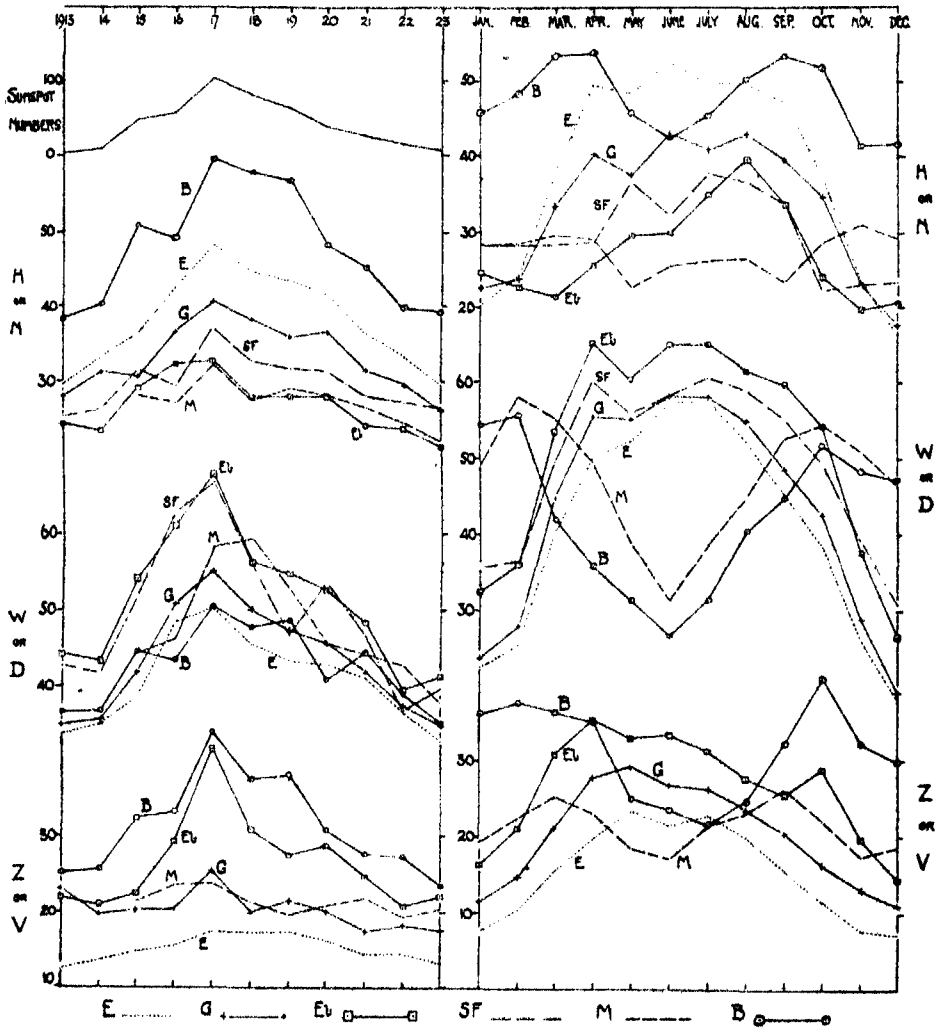


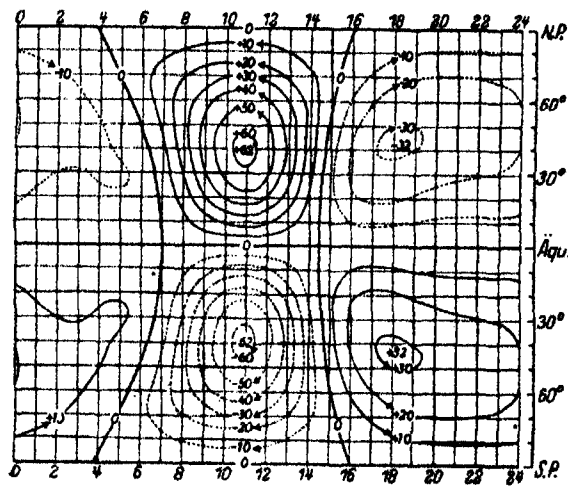
FIG. 1.—Solar Cyclic Variation of R.

FIG. 2.—Annual Variation of R.

curves for E and G, for which the values of $\bar{R}$ (not repeated here) were given in Tables I, II of our former paper; those tables also indicate the number of days involved in each mean value, though only approximately, because the number is not the same for every observatory and element, owing to occasional loss of record or (for M) unavailability of data.

4.1. The values of $\bar{R}$ may usefully be discussed in relation to the system of overhead electric currents that could, and probably does, produce the quiet-day solar diurnal magnetic variation S_q . But reference to these currents need not imply the adoption of any particular hypothesis concerning the physical cause of the daily magnetic variation; if desired, the diagram of the equivalent current-system may be regarded merely as a simple and convenient representation of the distribution of the magnetic-variation field.

The diagrams of the current-systems, reproduced here as figs. 3 and 4, are



due to J. Bartels.* They were constructed in accordance with S. Chapman's† spherical harmonic analysis of the S_q field (for a sunspot minimum year, 1902), and are therefore somewhat idealised; in particular, the variations were supposed to depend only on local time, the obliquity of the earth's magnetic axis being neglected. Hence in comparing results for our six observatories with this diagram, the magnetic rather than the geographical latitude of the observatories should be borne in mind.

Fig. 3 refers to the equinoctial period, and fig. 4 to the northern summer. The diagram for the northern winter is obtainable by inverting fig. 4 about the equator. The lines and arrows in these diagrams indicate the direction of flow of current, and are drawn at intervals such that between adjacent lines the current-flow is 10,000 ampères. The circles of latitude, and meridians, are indicated by straight lines, and the latitude and *local* time are shown; the middle meridian, numbered 12, refers to noon. The current-system is stationary relative to the meridians of local time, *i.e.*, relative to the sun. The currents fall into four divisions, two in each (north or south) hemisphere at the equinoxes, though at the solstices the systems in the summer hemisphere invade the winter hemisphere also. In each hemisphere one set of currents is situated in the sunlit region, and the other, which is weaker but more extensive, extends over the night and part of the day region. The total current in each day system at the equinoxes is 62,000 ampères, and in the summer day system, 89,000.

In considering these diagrams, the magnetic field at a point *below* the current-sheet, as at the earth's surface, must be imagined.‡ Its horizontal component will be nearly at right angles to, and to the right of, the local direction of current, being northward when the current is eastward, eastward when the current is southward, and so on; and its intensity will be nearly proportional to the local current-intensity, which is indicated by the spacing of the current-lines, regard being had to the distortion of lengths in the map-projection used. The vertical component of the field is less easy to gauge from the diagram, because it depends not on the local current-intensity, but rather on the rate of space-variation of this current-intensity; however, it will have its maximum near

* J. Bartels, 'Naturwiss.', vol. 18, p. 305 (1928), or 'Handbuch exp. Physik,' vol. 25 (1928).

† S. Chapman, 'Phil. Trans.,' A, vol. 218, p. 1 (1919).

‡ This magnetic field also contains a part due to currents induced in the earth by the outer current system. The internal currents increase the H and decrease the V components of the field of the outer currents, and alter the phase slightly; but in forming a general picture of the field, the inner currents may be ignored.

the foci, where the current-lines shrink to a point, and in the day current-systems it will be opposite in sign to the V component of the main field.

Further, to understand how the nature of the daily variations in the three elements at any station may be inferred from the diagram, the station must be imagined to move along a circle of latitude, from one local midnight to the next, and the variation in each element of the field during this passage, as indicated by the diagram at each point, must be noted.

4.2. The mean ranges for the elements at the six stations are as follows :—

Table VII.

Station :	E.	G.	Eb.	SF.	B.	M.
$\bar{R}$ (N)	38	33	27	30	48	27
$\bar{R}$ (W)	41	43	51	49	42	48
$\bar{R}$ (V)	15	20	26	—	31	21

If fig. 3 were exact, $\bar{R}$ (N) should have a maximum at the equator, decreasing thence, at first slowly, to a low value near the current-foci, in latitude $\pm 40^\circ$ approximately. With further increase of latitude, $\bar{R}$ (N) should again increase. This is borne out by Table VII ; $\bar{R}$ (N) is greatest for B, the station nearest the magnetic equator, and is least for Eb, SF and M, which are nearer the foci ; on going further northward to G and E, $\bar{R}$ (N) increases again. The minimum value, at Eb, is relatively higher than fig. 3 would suggest ; this may be due to the obliquity of the earth's magnetic axis. It may be noted that at about 11h. (the longitude of the foci), N should have its *maximum* at stations *between* the foci, and its minimum at stations beyond them ; the other extreme should come in the night hours, and be somewhat indefinite.

The range in $\bar{R}$ (W), according to fig. 3, should be greatest in the latitude of the current-foci, where $\bar{R}$ (N) has its minimum ; this is borne out by Table VII. From the latitude of the foci, $\bar{R}$ (W) should decrease to north and south, but more so in the equatorial direction, because at the equator the daily variation in W changes sign, and $\bar{R}$ (W) should vanish. The field is not sufficiently simple and regular for this to happen ; the reversal of the W-variation is effected through irregular transition stages in which $\bar{R}$ (W) does not vanish. Thus it is not much less at B than at Eb.

Again, $\bar{R}$ (V) should vary like $\bar{R}$ (W), and this is roughly so in Table VII, except that its value at B is unexpectedly large.

The values of $\bar{R}$ (V) are throughout smaller than those of $\bar{R}$ (N) and $\bar{R}$ (W) ;

this is because of the influence of the field of the internal induced current-system, already referred to in a footnote (§, p. 676).

Though $R(W)$ and $R(V)$ are similarly distributed in latitude, the daily variations of W and V are very different; V attains its minimum at about 11h., the longitude of the current foci, while its maximum is a very flat one, the variation at night being small; W has its minimum at about 8 a.m., and its maximum at about 2 p.m.

The Solar-cyclic Variations of Range.

5. Fig. 1 shows that the variation from year to year of the annual mean range R throughout the sunspot cycle is by no means parallel at all stations and in all elements. The annual mean sunspot numbers are indicated by the uppermost curve; sunspot maximum occurred in 1917. All the R curves also have their maximum in this year, except that for $R(MW)$. But in several cases the rise to and decline from this maximum is accompanied by secondary maxima and minima that have no counterpart in the sunspot curve. Some of these features are open to doubt; for example, the minimum in 1916 in $R(H)$ at SF is not paralleled at the adjacent station Eb, and likewise for the 1919 minimum in $R(W)$ at SF. The 1917 maximum of $R(Z)$ at Eb is unexpectedly outstanding.

The following table indicates the extent of the solar-cyclic variation of R ; it gives the difference between $R(\square)$ and $R(\sqcup)$, the mean values of R during the $\square$ and $\sqcup$ years of high and low sunspottedness (§ 3), expressed as a percentage of $\bar{R}$, the mean of R over the whole period.

Table VIII.—Values of $100 \{R(\square) - R(\sqcup)\} / \bar{R}$.

Element :	N.	W.	V.	Mean.
E	49	42	31	41
G	41	47	25	38
Eb	22	27	26	25
SF	17	23	—	(20)
B	27	20	33	27
M	13	20	7	13
Mean	28	30	24	27

The “means” in the table were derived from individual values taken to one more decimal place than is there given.

The mean sunspot numbers for the $\square$ and $\sqcup$ groups of years were respectively 70 and 16; or 70 and 21 for M, owing to the lack of two $\sqcup$ years 1913,

1914. The small solar cyclic variation at *M* is partly due to this smaller difference in mean sunspot numbers for the two groups of years. But the table suggests that it is also partly due to accident or local peculiarity. On the whole *W* seems to be the element having the largest solar cyclic variation, and the higher-latitude stations seem more affected than the lower latitudes ; but the table is insufficient to establish the reality of these differences, which would require much more data, for several sunspot cycles.

To determine whether $\bar{R}$ is systematically different in years of similar sunspot number, but in the ascending and descending phases of the solar cycle, the two groups of years 1914-1916 and 1919-1922 (mean sunspot numbers 38 and 35) were compared. The sum of $\bar{R}$ for all elements and the five stations *E*, *G*, *Eb*, *SF*, *B* (1914 for *M* not being available) was formed for each group of years ; the values obtained were 489·9 and 488·7, showing that $\bar{R}$ was practically identical in the two cases. Thus $\bar{R}$ appears to be slightly greater, for equal sunspot numbers in the descending phase, but the difference is too small to be certainly real. The conclusion to be drawn on this evidence is that *R* depends substantially on the mean sunspot number independently of whether this refers to the ascending or descending phase of the cycle.

Similar sums of $\bar{R}$ were formed for the three groups of years (1913, 1923), (1914-1916, 1919-1922), (1917, 1918), of mean sunspot numbers 3·6, 36·5, 92·7 ; they were 411·3, 489·4, 600·2, the corresponding mean *R*'s being 29·4, 35·0, 42·9. The successive differences between these (5·6 and 7·9 γ) divided by the corresponding successive differences of mean sunspot numbers (33 and 56) gave 0·17 γ and 0·14 γ as the mean rate of increase of the mean $\bar{R}$, per unit increase of sunspot number. Thus the rate is rather less in years of low than of high sunspot number, but the similarity of the two rates, 0·17 and 0·14, is more noteworthy than their difference. For a change of sunspot number by 100, $\bar{R}$ increases by about 15 γ , which is about 40 per cent. of the mean *R* over the whole cycle (about 35 γ), for these five stations.

It may be added that mean values of *R* corresponding to the last three columns of Table V were formed for *E*, *Eb*, *B* and *M* (and for all the elements there registered), using only *isolated* quiet days (§ 3). No significant differences from the values given in Table V were disclosed.

The Seasonal Variations of Range.

6. The mean ranges in the three seasons *ns*, *e*, *w* (§ 3) are as follows :—

Table IX.

Station :	E.			G.			Eb.			SF.			B.			M.		
Season :	ns	e	w	ns	e	w	ns	e	w	ns	e	w	ns	e	w	ns	e	w
R (N)	50	43	21	41	37	22	34	26	22	36	28	24	46	53	44	25	28	39
R (W)	55	44	23	57	48	25	63	58	33	56	54	35	32	44	51	32	44	51
R (V)	22	16	8	26	21	13	31	30	18	—	—	—	24	36	34	20	24	20

This table shows larger ranges in summer than in winter for the four northern stations, as was to be expected, but the two southern stations do not in all cases show the largest range in the southern summer (northern winter w), namely in R (BN), R (BV) and R (MV). Since B and M are in lower (southern) latitudes than the lowest-latitude northern station SF, their seasonal changes should be smaller; the fact that they are not always in the expected *direction* is probably due to the seasonal shift of the current-foci (*cf.* figs. 3, 4), which particularly affects the seasonal variation at the stations between them. The present stations are not sufficiently closely spaced, however, to give a clear indication, by the seasonal means of R, of the seasonal movement of the foci, or of whether the seasonal changes at a station depend more on its geographical than on its magnetic latitude.

The curves in fig. 2 show that the seasonal changes in R at the individual stations are not so regular as might be expected. The curious reduction in R (W) in May, already noted in our former paper for E and G, is now seen to be paralleled also at Eb and SF; but at these two stations R (N) does not share this May minimum, as it does at E and G.

Some of the irregularities in the curves of figs. 1 and 2 may be due to errors of measurement, especially in the case of N and V, the measurement of which involves temperature corrections which are not always certainly known. But the R (W) data should be reliable, and the May minimum of R (W), independently shown by E, G, Eb and SF, is evidence of this. The irregularities in figs. 1 and 2 must at least in large part be real, and show that the quiet-day diurnal magnetic variation S_q is not a really simple phenomenon.

The difference between R in summer (northern or southern, according to the station) and R in winter is shown in Table X as a percentage of the mean R.

Table X.

Element :	N.	W.	V.	Mean.
E	76	78	93	82
G	58	74	65	66
Eb	44	59	50	51
SF	40	43	—	(42)
B	— 4	45	32	24
M	15	68	0	28
Mean	38	61	(48)	49

This table well shows the natural increase, with increasing latitude, of the proportional seasonal variation. The " means " in Table X may be compared with those in Table VIII, which likewise show an increase with latitude. The figures of Table VIII refer to a sunspot-number difference of 54 (except at M), and for a sunspot-number difference of 100 (corresponding to the change from sunspot minimum to a considerable though not extreme sunspot maximum) should be nearly doubled ; they would then be very similar to those of Table X.

As in Table VIII, R (W) has the largest percentage variation ; the *seasonal* variation of R (V), however, exceeds that of R (N), whereas the opposite is the case for the solar-cyclic variation.

The Normal Range R_n , and the Ratio R/R_n or ρ .

7. As in § 12 of our former paper, the next step was to construct curves representing the normal range, for each element at each station, for all days throughout each year. From these curves the normal value of the range, R_n , was read off for each of the 819 quiet days included in the investigation. The ratio $\rho \equiv R/R_n$ of the actual to the normal range forms the basis of the further discussion. This takes the place of the quantity ΔR , equal to $100(R - R_n)/\bar{R}$, discussed in our former paper ; not only is ρ more easily calculated than ΔR , but it is also slightly preferable as a measure of the departure of the daily range from its normal value ; $\rho = 1$ represents normality, and $100(\rho - 1)$ the percentage departure from normality.

The Mean Values of $100|\rho - 1|$.

8. The degree of irregular day-to-day variability of R may be illustrated by Table XI, which gives the mean values of $100|\rho - 1|$, or the mean numerical percentage departure of R from its normal value, for various subdivisions of the data. The E and G data of our former paper were recalculated in terms of

ρ in order that the results for them might be given in a form strictly comparable with that of the results for other stations.

Table XI.

Station :	E.			G.			Eb.			SF.		B.			M.		
Element :	N	W	V	N	W	V	N	W	V	N	W	N	W	V	N	W	V
ns	14	14	21	17	14	19	20	13	17	23	17	16	23	23	21	25	23
e	15	15	22	17	14	20	23	14	17	26	18	16	21	21	18	28	22
w	24	23	32	25	21	25	22	18	22	22	20	19	23	21	26	24	30
☐ years	17	18	25	19	17	21	21	14	19	24	19	16	22	21	21	23	25
☐ „	18	17	25	21	16	22	23	16	18	24	17	17	23	23	23	29	25
0.0 days	18	17	23	21	16	20	22	15	19	23	18	16	23	24	21	25	26
0.1 „	18	18	27	20	17	21	21	15	18	24	19	17	23	22	22	26	25
All	18	17	25	20	16	21	22	15	19	24	18	17	23	22	22	26	25

The most notable feature of this table is the comparative uniformity of the values of $100 |\rho - 1|$ for all elements, stations, years and types of day (more or less quiet, 0.0 or 0.1).

Considering the latter first, the 0.1 days show a mean excess of only 0.4 in the mean of all elements, seasons and stations ; the corresponding difference for the three seasons separately (northern or southern) summer, equinox and winter, are 1.7, 0.8 and - 0.7, implying slightly reduced variability for the 0.1 days, as compared with the 0.0, in winter ; this is opposite to the indication from E and G alone obtained rather differently, in § 10 of our former paper. The main point, however, is that the 0.0 and 0.1 days are practically equivalent as regards the irregular variability of R.

The irregular variability of R is also practically independent of the mean sunspottedness ; the mean $100 |\rho - 1|$ is indeed less for the ☐ than for the ☐ years, but the difference, 1.1, is scarcely significant.

Combining all elements, and certain adjacent stations, the following are the seasonal means of $100 |\rho - 1|$:—

E + G.			Eb + SF.			B.			M.		
ns	e	nw	ns	e	nw	ss	e	sw	ss	e	sw
16.5	17	25	18	20	21	21	19	21	27	23	23

The irregular variability seems to be greatest in winter, and the more so, the higher the latitude ; at B, in a low latitude, the difference is imperceptible, while at M the change is in the opposite direction. Thus, except at E and G (which confirm one another in showing a considerable seasonal change) the variability is nearly uniform throughout the year.

The last row of Table XI shows that at the northern stations R is least variable in the element W, but at B and M this is not so. Averaging over all stations, the mean values of $100 | \rho - 1 |$ for N, W and V are 20·5, 19·0, 22·4, which are nearly equal.

For the six observatories separately (all elements being combined) the mean values of $100 | \rho - 1 |$ are as follows :—

E	G	Eb	SF	B	M	All
20	19	19	(21)	20	24	20·6

The differences here shown are insignificant.

Thus the main conclusion is that the average percentage departure of R from its normal value is approximately 20, nearly the same in all the circumstances considered. This conclusion was confirmed also when, as in § 5, the isolated quiet days (§ 3) were examined separately from the others.

The Constancy of the Type of the Quiet-Day Diurnal Magnetic Variation.

9. In our former paper we showed that the average *type* of the S_q variation is substantially identical, in all three elements, on days of small, average, and large range, the only difference being one of *scale*. This was demonstrated by a diagram (fig. 4 of that paper) referring to June and July at Eskdalemuir. It seems desirable to show that the same applies to at least one other station in a widely different latitude ; hence fig. 5 has been drawn, for Batavia, for the same months (which at B are in *mid-winter*). The three groups of days have been chosen according to their values of ρ ; the lowest curves represent the difference between the curves for the groups of largest and smallest range ; since they are nearly of the same type as the others, it follows that the curves of largest amplitude are approximately merely magnified versions of the upper curves. This is illustrated in another way by the similarity of the ratios (average departure)/range for the three mean inequalities for each element (Table XII) ; except in W (or —E) this is very close.

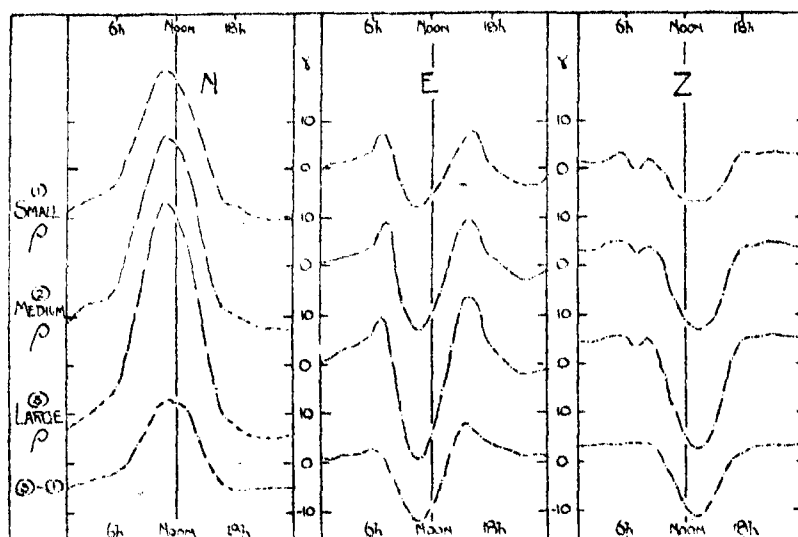


FIG. 5.—Diurnal Variations on Quiet Days at Batavia grouped according to ρ , June–July, 1913–23.

Table XII.

Element.	Group of days.	Number of days.	Range of mean inequality.	Average departure.	R/A.d.
N	Small ρ	53	30.9	9.1	3.4
	Medium ρ	53	39.2	11.6	3.4
	Large ρ	50	48.8	14.3	3.4
E	Small ρ	52	15.3	3.4	4.5
	Medium ρ	52	22.6	4.5	5.0
	Large ρ	52	33.2	6.2	5.4
Z	Small ρ	51	10.1	2.9	3.5
	Medium ρ	55	17.2	4.9	3.5
	Large ρ	50	28.6	6.7	3.5

Together with the curves already drawn for Eskdalemuir, this appears to provide adequate proof of the substantial constancy of type of the S_e variation, whatever its departure from the normal range, at all stations in low and middle latitudes. This constancy of type appears to have been first recognised by Moos,* in regard to the daily magnetic variation at Bombay.

On individual quiet days, however, in any of the three classes, there are

* N. A. F. Moos, 'Colaba Magnetic Data,' 1846-1905; Part II, 1910, § 587, p. 771.

small but appreciable departures from the average type. In particular, the maximum and minimum may occur earlier or later than the average, by an hour or more. This results in, and may be inferred from, a difference between the range of the average curve for any class of day, and the mean of the ranges of the curves for the individual days of the group; the latter mean is, of course, the greater, its values in the various cases being as follows:—

Station :	E.			B.		
	N.	W.	V.	N.	W.	V.
Small ρ	41.3	47.0	16.2	33.7	19.7	15.0
Medium ρ	51.1	57.5	21.5	41.6	27.3	21.9
Large ρ	58.1	67.0	29.0	54.9	39.5	30.0

These are greater than the ranges of the average curves for E and B by the following amounts:—

Station :	E.			B.		
	N.	W.	V.	N.	W.	V.
Small ρ	2.7	5.1	3.0	2.8	4.4	4.9
Medium ρ	6.0	3.1	2.6	2.4	4.7	4.7
Large ρ	4.8	2.1	3.5	6.1	6.3	6.4

The average percentage difference is about 10 per cent. of the mean range for E, and 16 per cent. for B.

The Change in R from one Quiet Day to the Next.

10. In § 3 it was shown that the very quiet days here considered tended to occur in sequences of two, three or more consecutive days. These sequences provide 352 different pairs of consecutive quiet days. We have examined the change in R from one day to the next, in each such pair; it is expressed by δR , defined by

$$\delta R = R_2 \text{ (2nd day)} - R_1 \text{ (1st day)}.$$

Table XIII gives mean values of δR , and also of $|\delta R|$, for various subdivisions of the data for the four stations E, Eb, B, M, the unit being 0.1 γ , and not, as elsewhere, 1 γ .

Table XIII.—Unit 0.1 γ .

Element :		N.						W.						V.					
Period :		ns	e	w	□	◻	All	ns	e	w	□	◻	All	ns	e	w	□	◻	All
E	δR	1	9	-12	-5	1	-1	14	7	-2	6	6	6	3	0	-4	-1	0	0
	$ \delta R $	65	57	55	65	56	60	84	72	51	80	63	69	59	38	31	49	40	43
Eb	δR	7	-2	-10	-9	3	-1	-5	7	-14	-4	-5	-5	4	0	-3	2	0	1
	$ \delta R $	81	70	63	82	66	72	84	72	62	78	70	73	60	56	40	59	48	52
B	δR	3	14	7	1	12	8	3	-7	27	18	2	8	7	-5	4	10	-3	2
	$ \delta R $	85	91	109	96	90	92	78	100	126	126	85	109	65	84	94	100	69	81
M	δR	-11	9	4	4	-4	0	18	4	21	16	13	15	5	1	15	14	0	7
	$ \delta R $	80	101	92	90	92	91	86	91	110	100	91	95	66	62	72	67	66	66

10.1. It is evident from Table XIII that $\delta R/|\delta R|$ is always small, so that the variation of R from one quiet day to the next is mainly irregular, and not systematic. The mean δR (combining all elements) for each of the four stations **E**, **Eb**, **B** and **M** has the values 0.2, -0.2, 0.6, 0.7 γ (mean 0.3 γ); combining all stations, the mean δR for **N**, **W**, **V** separately has the values 0.1, 0.6, 0.2 γ . The separate elements and seasons show some larger values, which are probably accidental; at any rate, much more data would be necessary to establish the reality of any such seasonal features. The main conclusion is that R does not alter systematically from one day to the next, in very quiet periods—apart, of course, from the slow regular seasonal and solar-cyclic variations, which, in the interval of one day, and in the mean for any of the three seasons considered, is unlikely to exceed 0.1 γ .

10.2. The most regular feature of Table XIII, as regards $|\delta R|$, is that, with one exception (**N** at **M**), each value for $\square$ exceeds the corresponding one for $\square$; this is natural, because in § 8 it was seen that the *percentage* variability of R is the same for $\square$ and $\square$, and since $\bar{R}$ is greater for $\square$ than for $\square$, $|\delta R|$ at $\square$ would be expected to exceed that at $\square$. But the increase of $|\delta R|$ from $\square$ to $\square$, expressed as a percentage of the mean $|\delta R|$, is somewhat less than that of R itself (Table VIII) in the mean for the same four stations; the means for **N**, **W** and **V** are 9, 22, 21 for $|\delta R|$ and 28, 27, 24 for R .

10.3. Ignoring the small difference between the values of R_n on consecutive days, we may write

$$\begin{aligned}\delta R &= R_2 - R_1 = (R_2 - R_n) - (R_1 - R_n) \\ &= R_n\{(\rho_2 - 1) - (\rho_1 - 1)\}.\end{aligned}$$

The values of $\rho - 1$ appear to be distributed approximately according to the law of errors (fig. 3 of our former paper shows this, for E and G, for the very similar quantity ΔR). If their values on consecutive quiet days are not connected with each other, but distributed just at random, the mean numerical value of $(\rho_2 - 1) - (\rho_1 - 1)$ is $\sqrt{2}$ times the mean value of $|\rho - 1|$; hence the mean value of $|\delta R|/\bar{R}$ should be approximately $\sqrt{2}$ times the mean value of $|\rho - 1|$. Actually it is distinctly less; the following are the values for the separate stations (all elements) and separate elements (all stations):—

	E.	Eh.	B.	M.	N.	W.	V.	All.
$100 \delta R /\bar{R}$	21	22	24	28	24	19	28	24
$100 \sqrt{2} \rho - 1 $	28	27	28	34	28	28	33	29

This indicates that the ranges on consecutive days have a slight tendency to depart from the normal range in similar directions.

10.3. This tendency has been further examined by calculating the correlation coefficients between the ranges on consecutive days, for the two stations E, B, taken as typical. The results were obtained for the separate seasons, and in some cases for $\square$ and $\sqcap$ years separately, but without disclosing any significant differences; consequently only the mean results are given here, as follows:—

E.			B.		
N.	W.	V.	N.	W.	V.
0.41	0.35	0.21	0.28	0.37	0.29

Out of the 818 days considered in Table II it was possible to form 137 sequences of three consecutive days (not all independent, in that, for example, a sequence of 4 days would afford two sequences of 3 days), 49 of 4 consecutive days, and 18 of 5 days. Correlation coefficients were calculated for the ranges on the first and last days of the sets of 3 and 4 days; again the separate

seasonal results showed no significant differences, and the mean results only are given, as follows :—

	E.			B.		
	N.	W.	V.	N.	W.	V.
1st and 3rd day	0.33	0.47	0.16	0.23	0.15	0.18
1st and 4th day	0.07	0.32	0.27	0.15	-0.03	0.15

These coefficients are based on rather restricted material, but with one (probably accidental) exception they are all positive and significant. They confirm the indication given by $|\delta R|$, that there is a tendency for the departures of R from the normal to show a moderate degree of persistence even to the 3rd or 4th day of a group of very quiet days.

Isotopic, Isomagnetic and Heterotypic Correlations.

11. In our former paper we considered two kinds of correlation between the values of ΔR on the *same* day ; our object was to find how far the departures of the range from its normal value were paralleled in different elements and at the two different stations E and G. In the present paper similar coefficients are considered in relation to the values of ρ , here taken as the measure of normality (or otherwise) of the daily ranges. The two kinds of correlation coefficients obtained may conveniently be called *isotopic* and *isomagnetic*, the former referring to correlations between different elements at the same *place*, and the latter to correlations between the same *elements* at different places. Later we shall also consider correlations between the values of ρ for *different* elements at *different* stations ; these coefficients will be called *heterotypic*.

Isomagnetic Correlations between Pairs of Adjacent Stations.

12. In our former paper (§ 16) we showed that the isomagnetic correlations between ΔR for E and G were very high for the elements N and W, namely, 0.77 for N and 0.84 for W ; for Z they were smaller, especially in winter—the seasonal and annual values were 0.65 (ns), 0.50 (e), 0.25 (w), 0.47 (y). The low correlation in winter is probably partly due to accidental errors of measurement, which will reduce the coefficient much more for Z in winter than for other elements or other seasons, because R (Z) in E and G is very small in winter.

In the present extended investigation we again have a pair of relatively adjacent observatories, Eb and SF, both situated near the current-foci of fig. 3, and hence in a distinctly different position from that of E and G. It is therefore of interest to examine the isomagnetic correlations for Eb and SF; this is possible only for N and W, as SF does not provide V data. The following are the results, which, though based on ρ and not on ΔR , are closely analogous to, and comparable with, the former results for E and G.

Season :	ns.	e.	w.	year.
N	0.73	0.56	0.65	0.64
W	0.72	0.70	0.65	0.69

These values show that in these elements the departures of the daily ranges from their normal values are on the whole very similar at the two stations, though not quite so similar as for E and G. But E and G are slightly closer together, both in latitude and longitude, than Eb and SF.

On account of this close magnetic correlation between *adjacent* observatories, it has been deemed sufficient, in forming other correlations not isotopic, to represent the pair of stations E and G by E alone, and the pair Eb and SF by Eb or SF.

Isotopic Correlations.

13. In our former paper (§ 17, Table IX) we determined the isotopic correlations between the ΔR 's for different elements at E, and also at G. The coefficients were found to be much smaller than the isomagnetic coefficients between the two observatories; the mean results were as follows:—

	NW	NV	WV
E	0.38	0.18	0.32
G	0.41	0.07	0.23

In order that the coefficients for E, taken as typical of both E and G, might be properly comparable with those from the further stations, new coefficients derived from ρ were calculated for E. They agree closely with those for ΔR , given above.

The following table contains seasonal and yearly (y) mean isotopic correlation coefficients for the various stations. To save space, the coefficients have been given in units of 0.01, as if they had been multiplied by 100.

Table XIV.—Isotopic Correlation Coefficients ; unit 0·01.

Elements :	NW.				NV.				WV.			
Season :	ns	e	w	y	ns	e	w	y	ns	e	w	y
E	34	47	32	38	25	11	15	17	32	32	37	34
Eb	34	33	21	30	8	3	11	7	32	43	44	40
SF	13	4	8	8								
B	15	19	28	21	6	14	16	12	51	65	73	63
M	-4	3	26	8	-12	-2	19	2	50	59	66	58

These results will be discussed, along with those of §§ 14, 15, in §§ 16, 17.

Isomagnetic Correlations between Distant Stations.

14. The following table contains the isomagnetic correlation coefficients for pairs of distant stations, for the seasons separately and combined. The difference of latitude between each pair of stations is indicated. Except in the first two cases (E, Eb and E, SF) there is also a considerable difference of longitude.

Table XV.—Unit 0·01.

Row.	Element :	N.				W.				V.			
	Season :	ns	e	w	y	ns	e	w	y	ns	e	w	y
1	E, Eb (15°)									9	10	12	10
2	E, SF (19°)	5	0	29	12	59	59	49	56				
3	E, B (61°)	15	16	6	12	2	10	-6	2	0	18	-5	4
4	E, M (75°)	11	5	10	9	2	7	-5	1	0	7	4	3
5	Eb, B (47°)	8	17	1	9	-2	5	-8	-1	2	14	6	8
6	Eb, M (61°)									-2	11	-3	2
7	SF, M (57°)	6	15	10	10	-2	3	-13	-4				
8	B, M (14°)	26	32	3	20	20	26	55	34	16	11	33	20

Heterotypic Correlations.

15. Six heterotypic correlation coefficients can be derived for each pair of stations. These have been calculated for the three pairs E and Eb or SF ; Eb and B ; B and M ; they are as follows. The first element of each pair in the heading refers to the first station of each pair in column 2 ; thus the first coefficient, 0·37, refers to N at E and V at Eb.

Table XVI.—Unit 0.01.

Row.	Elements :	NW.				NV.				WV.			
	Season :	ns	e	w	y	ns	e	w	y	ns	e	w	y
1	E, Eb	.	.	.	.	37	38	40	39	19	29	25	24
2	E, SF	47	46	37	43	.	.	.	.	.	.	.	.
3	Eb, E	27	30	14	24	18	30	17	22	32	8	11	17
4	Eb, B	-5	-9	16	1	-11	-9	13	-2	2	7	7	5
5	B, Eb	17	22	4	14	11	15	-1	8	1	9	1	4
6	B, M	10	13	19	14	6	21	19	15	17	22	42	27
7	M, B	4	-13	7	-1	16	-11	5	3	19	19	41	26

The following coefficients are for the elements N and W only, for more distant pairs of stations. The correlations relating to V for these pairs have not been calculated.

Table XVII.—Unit 0.01.

Elements :	NW.				WN.			
Season :	ns	e	w	y	ns	e	w	y
E, B	3	14	3	6	15	25	10	17
E, M	-14	8	4	-1	19	4	7	10
Eb, M	-14	-9	13	-3	.	.	.	.
SF, M	.	.	.	.	6	13	11	10

Discussion of the Correlation Coefficients.

16. Perhaps the most important feature in Tables XIV to XVII is the overwhelming excess of positive over negative coefficients. The following are the numbers and the sums of the positive (and zero) and negative coefficients of the three kinds in these tables.

Table XVIII.

	Number.		Sums.		Mean (unit 0.01).
	+	-	+	-	
Isotopic	49	8	1367	18	26
Isomagnetic	61	11	877	51	11.5
Heterotypic	82	14	1398	103	12.5
All	192	28	3642	172	16

Further, not a single "yearly" correlation coefficient (that is, one derived from all the ρ 's for a particular correlation) is negative by so much as -0.1 . It is therefore clear that there is a definite tendency on quiet days for departures of the daily range from the normal to have the same sign at all the stations and in all the elements here considered.

This conclusion is important in itself, and also in relation to the possibility* of developing a practical plan for the assignment to each Greenwich day of an index of the intensity of S_e on that day. In a later paper this possibility will be considered in detail.

The Correlation Diagram.

16.1. The correlation coefficients for the separate seasons are given in the tables in order to indicate the degree of regularity and reliability of the coefficients; on the whole, the differences between the seasonal values cannot be regarded as significant. Hence the discussion will be confined to the yearly means. These are illustrated diagrammatically in fig. 6. Here each observatory is represented by three points, one for each element (for SF the one for V is missing) on a horizontal line; the separation

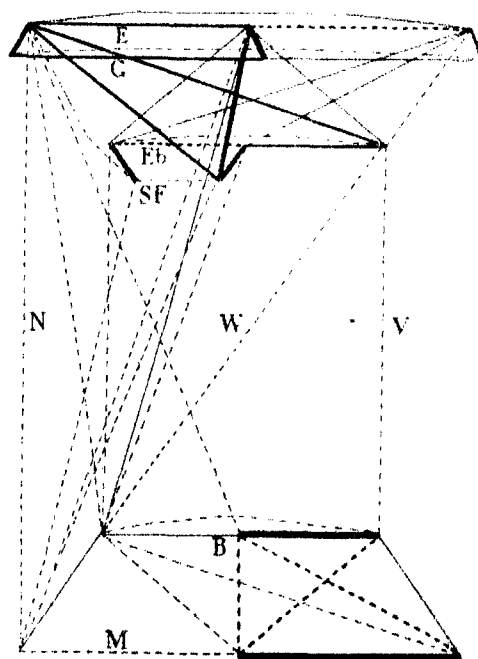


FIG. 6.

* Cf. Chapman, 'Nature,' vol. 121, p. 989 (1928), and § 19 of our former paper.

between these lines is proportional to the difference of geographical latitude between the corresponding observatories. On each horizontal line the three "representative" points, from left to right, represent N, W, and V; the spacing of these three points on the line is not the same in all cases, but this is merely for convenience and has no numerical significance. The lines joining the respective points, whether for the same element or observatory or not, indicate the correlation coefficients between the corresponding sets of values of ρ , to the nearest 0.1, in cases when the coefficient is (to this degree of accuracy) 0.1 or more; the absence of a connecting line in some cases (16 in number) denotes that the coefficient has been found and is less than 0.1, but in other cases, particularly for the lines joining the V points to the N or W points for the four pairs of stations considered in Table XVII, the coefficients have not been calculated. Thus the diagram, if complete, might show still more correlations than it now does.

The coefficients 0.1, 0.2, 0.3, 0.4, ... are denoted respectively by a thin broken line, a thin full line, a thick broken line, and by thick full lines of increasing thickness for the higher coefficients. The isotopic NV lines are necessarily not straight.

It is obvious from the diagram that the correlations are in general closer, the nearer the observatories; thus (apart from the adjacent pairs E and G, and Eb and SF, which show a high degree of correlation) E and Eb or SF, and B and M, naturally show a closer relationship than the more widely separated pairs such as Eb and B.

16.2. As regards the isotopic correlations, the low values for (N, V) are noteworthy; the isotopic (N, V) correlation is highest at E, the highest-latitude station; the decline is already considerable at G (as shown by the ΔR coefficient—§ 12).

The isotopic (N, W) correlation is very small at SF and at M; these are the stations nearest the current foci. The correlation appears to have a maximum between the foci (*cf.* the B value), and greater maxima beyond the foci on the poleward sides; thus for G the correlation (derived from ΔR) exceeds that for E and Eb; the sharp decline from Eb to SF is noteworthy, but may be accidental.

The isotopic (W, V) correlation is everywhere appreciable, and increases to high values (0.6) at B and M, the two stations between the foci.

16.3. The isomagnetic correlations in Table XV are, in the mean (*cf.* Table XVIII) slightly lower than the heterotypic correlations that have been calculated; but the highest isomagnetic coefficient (0.56, for E, SF; W) exceeds

the highest heterotypic coefficient (0.43, for EN, SF W). Though W has the largest isomagnetic coefficient, the W coefficients for pairs of observatories on opposite sides of the equator are definitely very small.

Apart from the two pairs of closely adjacent observatories, there are six correlations of magnitude 0.3 or more; two are isomagnetic (both for W, namely, E, SF; and B, M), and four are heterotypic (EN with SF, W and EbV, and BW, MV; BV, MW). There are seven correlations of magnitude 0.2, of which two are isomagnetic (B, M for N and also for V) and five heterotypic; of the latter the most interesting is that between EW and BN (this is strictly 0.17, slightly less than 0.2).

The Physical Significance of the Correlations of Range.

17. The correlations will finally be discussed in relation to the form and intensity of the current-system (figs. 3, 4) to which the S_q field may be attributed, and also in relation to the physical cause of the day-to-day variability of the S_q field.

(a) The fact that the correlations are positive throughout, even for the most widely separated stations, indicates a degree of parallelism in the day-to-day variations of range at different places distributed over the earth, which is most naturally interpreted as due to some *world-wide* cause affecting S_q , and varying in intensity from day to day.

(b) The fact that the non-isotopic correlations are fairly high for stations 5° apart, lower for stations 15° apart, and small for more distant pairs; and also the smallness of most of the isotopic correlations, indicate that there are also local causes affecting S_q , varying from day to day, but by different amounts in different places. These causes may be called regional, because they are fairly uniform over distances as great as 15° :

(c) The constancy of type of the S_q variations throughout the changes of range, in each element and at each station, as illustrated for Batavia by fig. 5, and for Eskdalemuir by fig. 4 of our former paper, indicates that the general form of the current-system (figs. 3, 4) remains unaltered throughout these changes. The current-system may suffer distortions or displacements, the current-lines may be crowded together in one place and spread out in another, but these irregularities of form and distribution are slight relative to the whole system; nevertheless their local magnetic effects may be comparable with those due to the general day-to-day changes of intensity of the complete system, wrought by the supposed world-wide cause.

17.1. These regional irregularities in the current-system may be ascribed to

similar irregularities in the distribution either of the electromotive forces (e.m.f.) or of the conductivity; but the former are likely to have much less influence than the latter; the flow round a circuit depends on the *integrated* e.m.f. round it, and local inequalities in the distribution of e.m.f. have little importance; but local inequalities of conductivity directly influence the local distribution of the current-lines, which crowd together to flow through a specially conducting patch, or spread away from a patch of low conductivity.

The conductivity depends on the ion-density, and therefore regional departures of ion-density from the normal value for each place and time seem to be the most probable cause of the regional irregularities in the distribution of the S_q ranges.

17.2. The world-wide cause partly governing the changes of S_q seems likely to be the solar ionising agency that produces the conductivity of the layer in which the current-system is situated (it may also play some part in producing the e.m.f.). Its intensity must vary from time to time, and if this cause acted alone, the S_q range in every element and at every station would vary in parallel with it, and correlations nearly equal to unity should result.

17.3. The cause of the *regional* irregularities of ionisation seems less likely to be directly solar; to suppose it *is* directly solar would imply that the intensity of the beam of solar ionising radiation varied patchily over the cross section, on a scale fairly small compared with the area of the earth. But the angle subtended by the earth at the sun is so very small that this patchiness of the beam is improbable, however irregular the distribution of emission might be over the sun's surface. One may instance the analogy of a beam of light falling on a sheet of paper from an electric lamp a few feet away; the curly filament of the lamp represents a highly irregular distribution of the emission, yet there is no perceptible non-uniformity in the illumination of the paper. Patchiness of emission might be more likely to survive in a solar beam if the radiation is corpuscular rather than wave-radiation, but here also it would almost certainly be obliterated by lateral diffusion of the corpuscles long before the beam reached the earth; for with any probable density of the stream, the mean free paths of the corpuscles would be at least of the order of a thousand kilometres, permitting rapid equalisation of density across the stream.

17.4. Thus the regional irregularities of ionisation or conductivity seem likely to be due to terrestrial causes. One can only speculate as to their nature; perhaps the most obvious possibility is as follows: an irregularly varying distribution of conductivity would be produced by a uniform solar

beam if the height-distribution of upper atmospheric air-density varies irregularly with latitude and longitude, as is the case in the lower atmosphere. The absorption of ionising radiation occurs in a layer whose situation and thickness, for a given solar beam, depend on the equivalent "homogeneous height H " of the atmosphere in the locality*; H depends mainly on the temperature. The number of ions produced per unit volume per unit time is proportional, for a point at any given fraction of the thickness of the layer above or below the level of maximum absorption, to $1/H$. If the coefficient of recombination is independent of the pressure (as may be the case at very low densities), the resulting ion-density in the steady state is proportional to the square root of the number of ions produced per unit volume and unit time, and therefore to $1/H^{\frac{1}{2}}$. The total conductivity of the layer is proportional to the density integrated through the thickness of the layer, and therefore to $H^{\frac{1}{2}}$. Actually the state is not steady, but nevertheless the actual total conductivity is likely to depend on H in a similar way, that is, as $H^{\frac{1}{2}}$. Thus an irregular distribution of upper-atmospheric temperature and density would lead to an irregular distribution of total conductivity. If the current system depends partly on drift currents instead of conduction currents, similar conclusions are likely to hold good, and the same applies also to the diamagnetism of the upper ionised layers.

17.5. The correlation of the daily abnormalities of range on successive quiet days (§ 10.3) implies that the regional inequalities of conductivity (or drift currents or diamagnetism) tend to persist from day to day. The actual conductivity dies away at sunset and is renewed after sunrise next day; the abnormalities of solar ionising intensity or of upper atmospheric conditions, or both, must therefore tend to persist from day to day.

17.6. A complete understanding of the changes of S_q would include a knowledge of why some of the correlations are so much larger than others (even in cases where no difference in distance is involved). We are unable to give a detailed explanation of this, but one point may be noted—the much lower correlation, with other elements at other stations, of the N range near the focus (i.e., at SF and, to a less extent, at M) than of the W and V ranges there. This seems natural because at the focus the S_q variation in N is reversed in type, through transitional stages of small range, whereas in W and V the range is near its maximum; thus local irregularities of conductivity near the focal latitude are likely to affect the range much more in N (especially propor-

* S. Chapman, 'Proc. Phys. Soc.,' vol. 43, p. 26 (1931).

tionately) than in W and V; consequently the N correlations, depending on the world-wide changes of conductivity, are the more blurred-out and reduced.

Summary.

The discussion of the range of the daily magnetic variation, on very quiet days, previously considered for the two stations Eskdalemuir and Greenwich, is extended to four more stations, Ebro, San Fernando, Batavia and Mauritius.

It is found that the ranges vary from day to day in an irregular way, and that there is a definite correlation between the changes in different elements and at different stations—the correlation being less, the more distant the stations.

It is found that the very quiet days often occur in sequences of two or more, and that there is a tendency for abnormalities of range to persist for two or more days.

OBITUARY NOTICES.

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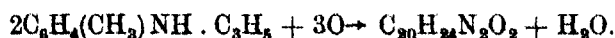
W. H. Perkin

WILLIAM HENRY PERKIN—1860-1929.

W. H. PERKIN was born at Sudbury, near Harrow, on June 17, 1860, and was the eldest son of William Henry Perkin, destined to become Sir William Perkin, the discoverer of the coal-tar colours. W. H. Perkin, the father, was, in 1856, acting as Assistant to A. W. Hofmann at the Royal College of Chemistry in Oxford Street, but his keenness was such that he had fitted up for himself a laboratory at home where he carried out experiments in the evenings.

It must be remembered that at that time the type theory of organic structure still held sway and although chemists generally realised that this theory could no longer be employed to explain the intricacies of organic structure, the structural theory, such as we know it to-day, had not been evolved and Kekulé had not yet put forward his explanation of the structure of benzene. Organic chemical research could, in those days, be carried on only by means of empirical formulæ and the only means of prediction lay in utilising the empirical chemical equation.

It was in 1856, that is three years prior to his marriage, that W. H. Perkin, senior, set himself the task of preparing the alkaloid quinine by the oxidation allyl toluidine in accordance with the equation



No quinine was, of course, obtained—as we know, from our modern structural formulæ, such a reaction is impossible unless it were accompanied by some molecular re-arrangement wholly without precedent. Nevertheless a black precipitate was produced in this reaction which Perkin found to contain a violet substance, subsequently to be prepared more cheaply and in better yield by the oxidation of aniline sulphate. This substance constituted Mauve or Aniline Purple which was the first of the coal-tar colours; the precursor of that vast series of compounds, the value of which now reaches many millions of pounds yearly.

Perkin, senior, despite the advice of Hofmann, decided to leave the Royal College of Chemistry and to start manufacturing the new dye on the large scale, an amazingly courageous decision when it is remembered that chemical manufacturing processes were then in a most rudimentary condition, and every type of plant necessary for the various operations had to be devised and erected and that, in many cases, the simplest chemical reagents had to be prepared or purified. Thus the benzene obtainable was unequal in quality and had to be fractionated. Nitric acid strong enough for making nitrobenzene could not be obtained commercially, and the nitration of benzene had to be done with a mixture of sodium nitrate and sulphuric acid. Nevertheless

such was the skill of the young chemist that within six months Aniline Purple was being manufactured in large quantities at the works at Greenford Green, which had been set up for the purpose. Soon the demand for the new colour became so great that the works had to be enlarged. It caught the popular imagination and was evidently a frequent subject of conversation at that period.

The younger Perkin was therefore born in an atmosphere of chemistry and breathed it from his earliest moments. A year after his birth, that is in 1861, his brother Arthur George was born, and shortly afterwards their mother died. It was not until six years later that W. H. Perkin, senior, married again, there being five children of the second marriage, four daughters and one son (the late Frederick Mollwo Perkin).

At the age of ten William Henry, junior, entered the City of London School, where a year later he was followed by his younger brother. The choice of this school by the father was not merely due to its being his old school but also because it was the only one he knew in which science found a place in the curriculum.

In those days there were remarkably few places in which systematic instruction in chemistry was given. In London there was but one place where this science alone was taught and that was the Royal College of Chemistry in Oxford Street, which owed its initiation largely to the Prince Consort, Sir James Clark, and Sir Lyon Playfair. It had no endowment and the funds necessary for the erection of the laboratories were obtained from a number of public-spirited men. Here under A. W. Hofmann and later, when he left to take up the post of Professor of Chemistry in Berlin, under Sir Edward Frankland, a long series of distinguished English chemists received their education.

In 1872 the College was transferred to the building in Exhibition Road, which, although providing much more space than the Oxford Street building, suffered from the disadvantage of not having been designed for chemical purposes. Its name was now changed to that of Royal College of Science.

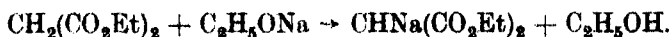
The younger Perkin remained at the City of London School from 1870 to 1877, living with one of the masters but spending the week-ends at Sudbury. Here their father had had fitted up for the two boys a shed at the bottom of the garden, in which was placed two benches, one for William, the other for Arthur. He did not teach them but gave them simple operations to do such as crystallisations and so forth. No doubt also the two brothers made frequent visits to the Greenford works, where a suitably equipped research laboratory had been erected and where much important work was carried out not only in connection with dyestuff chemistry but also in other fields in which the elder Perkin was interested. It was here that he first made the acquaintance of Alexander Pedler, who was then an assistant in the laboratory.

In 1874 the Greenford works were disposed of to the firm of Brook, Simpson & Spiller, and Sir William Perkin built for himself a new house in the garden

at Sudbury, whilst the old house was converted into a laboratory, in which he devoted himself to research.

In October, 1877, Perkin entered the Royal College of Science—the Chemistry Department being then under Sir Edward Frankland. Mr. A. J. Greenaway, who was at that time a demonstrator in the College, tells how Perkin was at once recognised as a man of exceptional manipulative skill and that he quickly worked through the preparation course. It was from here that he published his first two scientific communications, one on the action of sodium on phenyl acetate, and the other on the action of benzyl chloride on phenyl acetate, both in conjunction with Dr. W. R. E. Hodgkinson, a lecturer in the College.

At this time the German schools of chemical research were in the hey-day of their fame. Great and fruitful schools had been established in Heidelberg, under Bunsen, in Munich, under Bayer, and elsewhere. It was clear that no chemical education could be complete without the experience and inspiration which could only be obtained abroad, and it was clear that one of our most promising younger chemists would have to undergo this training if he were to make full use of his powers. Consequently in 1880 Perkin went to Würzburg, to work under Johannes Wislicenus. Here he took his Ph.D. degree in 1882, presenting as his thesis the work he had carried out on certain condensation products of oenanthaldehyde. It was during this period that Perkin first became interested in the properties of substances of the ethyl malonate and ethyl acetoacetate type, the interest being aroused because two pupils of Wislicenus, Conrad and Limbach, had just previously shown that the sodium derivatives of these substances could be prepared by a process of double decomposition from sodium ethoxide



Probably few organic research chemists have used more of these materials in their research work than Perkin.

In the autumn of 1882 Perkin went to work under Adolf Bayer at Munich, and entered on what may be regarded as the first most fruitful period of his career.

Bayer's laboratories at Munich had only been completed some four years previously, and were so well designed that they long served as a model for the other laboratories which were springing up in all the principal university towns in Germany.

Perkin has left on record in his Bayer Memorial Lecture the affection and devotion he felt for this great master. As a matter of fact the two men were singularly alike, and a great deal of what Perkin says of Bayer might equally well be said of Perkin himself. There was obviously a strong bond of sympathy between master and pupil—sympathy based on similar outlooks and similar ideals. Both were experimenters of the very highest order, and both were very

careful before drawing any theoretical conclusions from the experimental data they obtained. Bayer, for example, worked for 17 years on the structure of indigo before he suggested a structural formula for it, and although nothing quite so meticulous as this can be ascribed to Perkin, yet it is certain that, when he has had all the necessary experimental details in his hands, he has been forestalled by others with less regard than he for the necessity of clear proof.

Both Bayer and Perkin were most effective when working on a small scale, and to watch Perkin at work crystallising some substance, of which perhaps not more than half a gramme was available after several weeks' work, provided a lesson well worth learning.

The laboratories at Munich were crowded with the most promising men from all parts of the world who came to study under Bayer. It was not often that Bayer suggested subjects for the research work which the Ph.D. candidates were carrying out for their theses. When fit for original work they were usually handed over to one or other of the many Privatdozenten attached to the laboratory. These Privatdozenten were often men of great experience, the post being obtained on the recommendation of the Professor after the candidate had presented a thesis. Perkin presented as his thesis the work he had done in the laboratory on benzoylacetic ester, the phenyl analogue of acetoacetic ester. This work had proved to be of a very tedious character because, in those days, the methods of distillation under reduced pressure had not been perfected and in consequence it was practically an impossibility to obtain an easily decomposable liquid of this kind in a state of purity. Perkin was successful in his application and was placed in charge of a large laboratory.

It was at this time that Bayer was completing his synthesis of natural indigo, and one of the chief difficulties was found to be the poor yield of the ortho compound obtained by the nitration of cinnamic acid. One morning, Bayer found on Perkin's bench a large quantity of *o*-nitrophenylpropionic acid, for the preparation of which the *o*-nitrocinnamic acid was required, and it appears that Perkin had solved the problem by nitrating not the acid but the ester, a discovery of the highest importance and one which ultimately rendered this method commercially practicable.

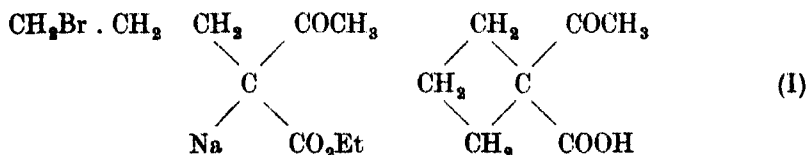
At this period Kekulé's theory of the structure of the benzene ring had found full acceptance and the existence and structure of the reduced compound cyclohexane was also agreed to. It therefore seems remarkable that the idea of the possible existence of rings containing a lesser or a greater number of carbon atoms than six was strongly resisted by the chief chemists of the day. This is all the more remarkable when it is remembered that the idea of carbon combined to carbon by more than one valency as in ethylene $\text{CH}_2 = \text{CH}_2$ was generally accepted, but it is evident that the connection between this structure

and that involving three carbon atoms $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} - \text{C} \end{array}$ could not then be seen.

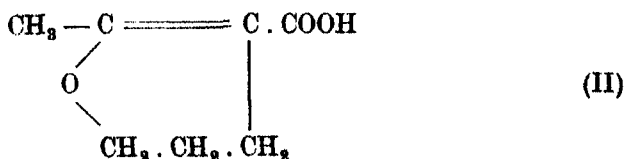
Moreover, substances like the γ -lactones and five rings containing nitrogen were already known. For some time previous to this Perkin had determined to institute experiments to test the validity of this assumption, but was strongly dissuaded from doing so by B  yer, by Victor Meyer and by Emil Fischer, all of whom regarded the project as waste of time. Indeed, Perkin told me that on one occasion Victor Meyer stayed so late arguing with him on this point that they had to spend the night together. Perkin also showed me a letter he had received from a distinguished English chemist, in which the passage occurs: "Perkin, you are going to make a fool of yourself, three-carbon rings do not exist."

Nowadays we know how right was Perkin's judgment, and the wealth of new knowledge which has followed in the wake of his initial discovery is well known. Three, four, and five-membered rings exist and a vast number of their derivatives are known. Moreover, Ruzicka has recently shown that rings containing many more carbon atoms are capable of isolation and indeed form the constituents of many natural products.

It is interesting to note that what was regarded as Perkin's initial success in this matter was wrongly interpreted by him. He had tried the action of the sodium compound of acetoacetic ester on ethylenedibromide and obtained a substance which he considered to be the compound (I).



This was generally accepted as correct and many of the doubters, including Victor Meyer, withdrew from their opposition and wrote Perkin charming letters of commendation. Some three years later Perkin himself discovered accidentally that this formula was wrong, and that the reaction had not led to the formation of a four-membered ring at all but to the substance (II)



that is to say, a six-membered ring.

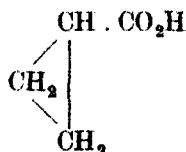
It is perhaps permissible to surmise as to what might have happened had Perkin originally interpreted the result correctly. Would this verification of his opponents' views have disheartened him and caused him to abandon the quest? As a matter of fact the false interpretation had so far encouraged him that, by the time he had corrected it, a very large number of similar

reactions had been carried out, the products of which were unquestionably cyclic? For example, if malonic ester is substituted for ethyl acetoacetate in the above reaction the product is undoubtedly the cyclic substance (III).



It is possible that discouragement might have ensued considering the character of the situation, but knowing the man I do not think it is at all likely. Nevertheless, the incident is of interest as showing that a mistake may sometimes have a beneficial result.

The real problem was whether the ring compounds prepared by Perkin were in fact unsaturated compounds. For example, Fittig maintained that the substance stated by Perkin to be



was, in reality, vinylacetic acid $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{COOH}$. This point was subsequently settled by Wislicenus who synthesised vinylacetic acid and found it to be different from Perkin's acid.

Perkin left Munich in 1886, but before passing from this period it is perhaps desirable to recall that, in later life, B  yer was wont to say that of all the distinguished men who had passed through his hands the two of the greatest ability were Emil Fischer and Perkin.

For the next year he was housed in the Owens College, Manchester, whither he had been invited by the late Professor H. B. Dixon, who had just succeeded Sir Henry Roscoe in the Chair of Chemistry. He then started his work on brazilin and h  matoxylin but abandoned this for a time on his appointment in 1887 to the Chair of Chemistry at the newly-founded Heriot-Watt College, Edinburgh. The Edinburgh period lasted four years and despite the difficulties entailed by evening teaching and poor accommodation much research work was done. This period is noteworthy for the fact that it saw the initiation of the work on the alkaloids, research on both berberine and cryptopine being started here.

In 1892 Perkin was appointed to succeed Schlorlemmer in the Chair of Organic Chemistry in the Owens College, Manchester, and entered on his second most fruitful period which he himself used to call his golden age.

It fell to Perkin's lot to establish a true school of organic research in Manchester—a school based on those with which he had become acquainted in

Germany and especially that of Bayer at Munich. From this school there emanated a steady stream of trained research workers, some passing into the industry, others into academic life. These latter started fresh schools of their own in the places to which they went and in consequence the seed sown throughout the country quickly germinated and if to-day we can say with assurance that our research schools in organic chemistry are in no way inferior to those abroad, either on the Continent or in America, it can be safely said that this highly satisfactory state of affairs is due to Perkin and to the example he set.

When the writer joined this school in 1896 it was already in full operation. The great Schlorlemmer Laboratory was crowded with students each vying with the other to further the work of the school, for it was Perkin's plan to concentrate on some particular field of research all the power at his disposal. It has been stated more than once by persons who have had little or no means of judging that Perkin exploited his students, that, for example, he used them as a means of preparing raw material which he subsequently took from them and worked on himself. That he gave them little or no chance of learning that fine technique of which he himself was a master. This is not true, and it were well that this mis-statement should be once and for all categorically denied.

It was my privilege to be intimately associated with Perkin for 14 years, that is from 1896 to 1910, and during that period I have never known him use a student for any purpose other than that required by his training. It is inevitable, of course, that a great deal of the large scale preparation work must fall on the student, but even so this kind of work given by Perkin to any particular student was only that related to the particular problem he had in hand, and to say that Perkin kept a number of research students busy doing nothing else but supplying him with material, the object of which was unknown to them, is totally untrue. As already stated elsewhere Perkin, like his teacher Bayer, was at his best when working on the small scale, and it is natural, therefore, that when a student has reached a point where a small quantity of material represented many weeks' work, Perkin should take the substance from him and submit it to that system of purification which could only be carried out by him and which, in the hands of the student, would have led to catastrophe. Even so, such operations were always carried out in the presence of the student who was able to see the marvellous manipulative skill of the man and was in a position subsequently to emulate him, as indeed many of his students did, with complete success.

At Manchester Perkin continued his work on braziline and hæmatoxylin and also on some of the alkaloids, but when the writer reached Manchester the chief object of investigation was camphor. At the same time much work was being carried out in related fields, because it was Perkin's wish not only to investigate any one substance directly but at the same time to carry out researches on many related side issues in the hope that ancillary matter might

prove of use in settling the main question. How true his insight was in this connection will be realised later when his research work on the Terpenes is discussed.

Camphor had proved itself to be an insoluble problem for some 10 years previously. The many different kinds of derivatives obtained from it rendered any discussion of its structure exceedingly difficult. Nevertheless the recognition of derivatives of succinic and glutaric acids among the products of degradation showed Perkin the necessity of studying closely the various compounds of this class.

The research work on camphor and related substances occupied the attention of Perkin's school until Komppa's synthesis of camphoric acid and subsequently of camphor settled the problem. Undoubtedly this synthesis came as a sad blow although Perkin was the first to telegraph congratulations to Helsingfors. The blow was all the more acute because the synthesis of camphoric acid had actually been achieved prior to the publication of Komppa's work, but the series of reactions had failed at the last stage and it was not possible to obtain sufficient camphoric acid for more than a mixed melting point determination. Subsequently when the work was repeated on a much larger scale the identity of the first product with camphoric acid was clearly established.

It is perhaps difficult for anyone not engaged in this kind of work to realise the acute sense of disappointment which is experienced when a whole series of reactions is rendered useless by failure at some particular stage. In this case no less than nine distinct operations had to be carried through. Each reaction gave a good yield and all seemed well until the final stage was reached in which it was only necessary to replace Br by CN. This, usually one of the simplest of all organic reactions, could not be brought about or could only be brought about in so small a degree as to render the quantity of the desired product too small for further investigation.

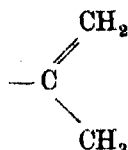
Perkin was an extraordinarily rapid worker and one of remarkably regular habits. He lectured on four mornings of the week at 9.30. Thereafter he worked until 12.15 in the laboratory, going to lunch punctually at the hour named. One o'clock saw him back at the bench, where he remained until four.

Although the laboratory rarely saw him at other times, he placed no restriction on the hours of work spent by his students and the laboratory was available at all hours of the day or night for any who cared to work therein. This privilege was taken advantage of by many and during term time one would frequently find students at work at 1 or 2 o'clock in the morning.

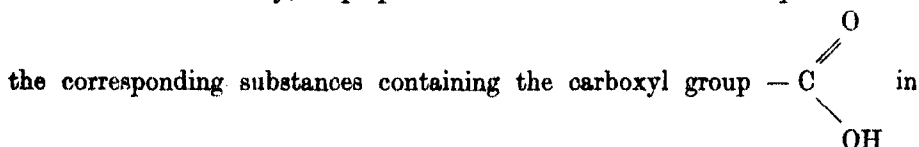
Perkin himself was a man of unbounded energy. Each occupation was carried out with a zest which showed that he put his whole soul into everything he did. Whether he was playing the piano (on which he was a great performer), digging in his garden (his cultivation of carnations brought him some fame),

playing tennis or cricket (he was no mean bowler), one only had to look at him to realise that he treated the occupation of the moment with the same seriousness and desire for achievement as he treated chemistry.

One of Perkin's chief triumphs during the Manchester period was his synthesis of the terpenes. These natural hydrocarbons, of which pinene is an example, are six-membered carbon rings, and Perkin, as has already been mentioned, knew all there was to know about substances of this type. What he did not know and could not possibly know was how to add the side-chain characteristic of the terpenes, a side-chain which may be expressed thus

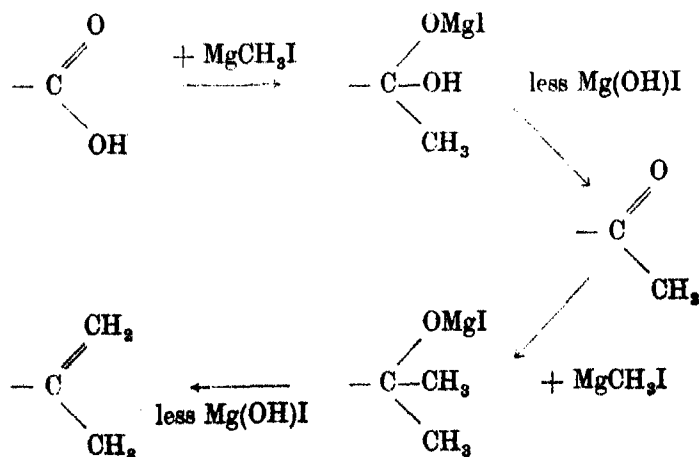


Nevertheless, with that extraordinary insight and intuition, which at times seemed almost uncanny, he prepared and laid aside considerable quantities of



place of the hydrocarbon residue, although he could then have had no possible hope that any reaction could be devised which would enable him to transform the one into the other.

Nevertheless, the apparently impossible happened and in the Grignard-Barbier reagent (MgICH_3), which was shortly afterwards discovered, he found the ideal substance and was able to transform the cyclohexane acids he had accumulated into the natural terpenes, so that now with the exception of pinene none of the simpler type remain to be synthesised. This amazing reaction can be represented thus :



There was nothing Perkin hated so much as to attend committee meetings, and although his advice was always sound and astute he felt, as many of us do, that a great deal of the time spent in this manner is wasted. In Manchester he was fortunate in having H. B. Dixon as his colleague, and thus to be relieved of a great deal of administrative work. But later, at Oxford, I have heard him complain bitterly of the time he was forced to spend away from his laboratory at University boards and committees. He acted as examiner on many occasions for various universities and institutions, and often visited them for the purpose of examining orally candidates for the Ph.D. degree. This last-named occupation always gave him the greatest pleasure, because it enabled him to get into touch with the younger men and to make himself familiar with the work being carried on in the institution he was visiting. For example, after an examination, he would ask to be shown round the laboratory and would discuss the major problems in hand with the men engaged on them. In 1912 the Waynflete Professorship of Chemistry at the University of Oxford became vacant owing to the death of Professor Odling, and Perkin decided to accept the invitation to occupy the Chair. This can only be described as a most courageous decision. Perkin was then 52 years of age, and had, as we have seen, established a school in Manchester, which was at the zenith of its fame and renowned the world over. To leave it and establish a new school in other surroundings must have required the exercise of great moral courage and a degree of personal confidence in his own power which is possessed by few. The developments in Manchester during Perkin's stay had been stupendous. Starting with very meagre accommodation he had designed and built the Schorlemmer Laboratory and the cellars underneath; the next extension had occurred when the laboratory of the late Dr. Schunck was removed brick by brick from Kersal Moor to a site adjoining the Schlorlemmer Laboratory. This addition provided Perkin with a private laboratory which was built between the old structure and the Schunck Library and gave increased accommodation for many years until renewed demands for space led to the building of the Morley Laboratory, an addition which nearly doubled the research accommodation available. In Oxford no such facilities existed, and it was clear that Perkin would have to establish and equip new laboratories there.

Fortunately he found in the person of Sir William Dyson Perrins one who was prepared to provide the necessary laboratories and to endow them. A stately building soon arose in which the experience gained by Perkin in Germany, Edinburgh and Manchester was embodied, giving a series of laboratories which are even now—15 years after their erection—probably unsurpassed so far as facilities for research are concerned.

It is of interest to note in passing the remarkable effect Perkin's removal from Manchester to Oxford had in the course of the next few years, excluding the war years, on the research output from the two places. This point arises

from data given by Professor W. P. Wynne in his Presidential Address to the Chemical Society in 1925, and it is of interest to reproduce his table. Professor Wynne takes the six-year periods, 1901-06, 1908-13, 1919-24, as being typical and compares the number of papers published in the chief chemical journals from *inter alia* Oxford University, Cambridge University, Manchester University, and the Imperial College respectively during those periods. The figures are very striking—

Distribution of Papers.

	1901-06	1908-13	1919-24
Oxford University	18	89	140
Cambridge University	82	122	142
Manchester University	91	139	84
Imperial College	101	114	143

It will be seen that whereas Cambridge University and the Imperial College show a steady increase, Oxford shows a leap forward after Perkin came in 1912, whereas Manchester shows a sharp fall after he left.

The Oxford period, which may be described as Perkin's third most fruitful period, led to the output of a great deal of research work mainly on the alkaloids. Definite steps forward were taken in the determination of the structure of strychnine and brucine and the synthesis of a number of complex compounds of the type, namely, cryptopine, protopine, epiberberine, harmine, oxyberberine, and others. In this and other work he carried out there he was fortunate in having the collaboration of Professor Robert Robinson, who has now succeeded him as Waynflete Professor of Chemistry.

Perkin, although a shrewd business man, did not devote much of his time or skill to commercial work. He once said that although he had made a vast number of new organic compounds he could not remember ever having made any which could be put to a useful purpose. Nevertheless, during the war period he served as Chairman of the Advisory Council to British Dyes, Ltd., and helped in the organisation of that firm to meet the demand for dyestuffs cut off by the war. Later, in 1924, he was appointed Director of Research and became also a member of the Board of Directors. He was also associated with the late Sir William Ramsay in developing a process for the preparation of synthetic rubber from butyl alcohol which, however, failed to be industrially practicable. It is strange that although brought up in close touch with the synthetic dyestuffs he never actually worked on them, and excepting in the use of butadiene rubber, to which reference is made above, and also in connection with "non-flam," a process for rendering fabrics non-inflammable, it is probable that his name never appeared on a patent specification.

He gave good service to the societies of which he was a member, and served

as President of the Chemical Society (1913-15) and as Vice-President for no less than 19 years. He served for two periods on the Council of the Royal Society (1904-05 and 1908-10). His literary activities were few but he found time to produce two well-known text-books in conjunction with Professor S. Kipping, one on inorganic and the other on organic chemistry. With Dr. Lean he also wrote a small introduction to Chemistry.

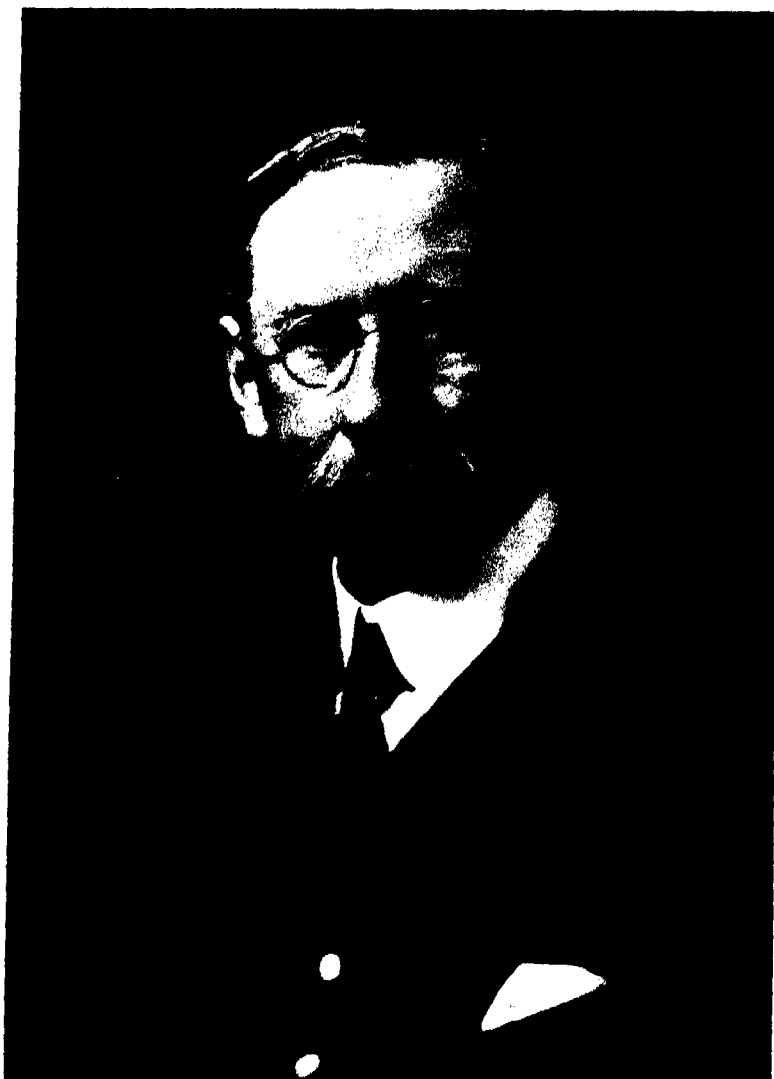
He was an able and fluent lecturer and those who were fortunate enough to take his courses rarely failed afterwards to speak of them in terms of the highest praise. He was especially lucid when explaining some of the more intricate portions of his science, and in describing sections in which he himself had laboured.

He received many honours. The Universities of Cambridge, Edinburgh, St. Andrews, and Manchester, conferred on him Honorary Doctorates, and he was Honorary Fellow of many learned societies. He was awarded the Longstaff Medal of the Chemical Society in 1900, and the Davy Medal of the Royal Society in 1904, and a Royal Medal in 1925.

In 1887 he married Mina, daughter of the late Mr. W. T. Holland, of Bridgewater, who survives him.

The writer of this notice wishes to express his thanks to Mr. A. J. Greenaway for having allowed him to use the manuscript of his Chemical Society notice. The writer has quoted freely from this, especially in connection with Perkin's earlier life with which Mr. Greenaway was so well acquainted.

J. F. T.



A. A. CAMPBELL SWINTON.

ALAN ARCHIBALD CAMPBELL SWINTON—1863–1930.

By the death of ALAN ARCHIBALD CAMPBELL SWINTON, on February 19, at his home, 40, Chester Square, London, scientific and industrial research loses one who did valuable work especially in X-rays and radio communication. The third son of A. Campbell Swinton, of Kimmerghame, Berwickshire, and Georgiana, daughter of Sir George Sitwell, Bart., he was born on October 18, 1863. From 1842 to 1862 his father was the professor of civil law in the University of Edinburgh. He also held the coveted post of Brigadier-General in the Royal Company of Archers, the King's Body Guard for Scotland. Professor Swinton's second son was Captain George S. C. Swinton, Chairman of the London County Council in 1912, and Lord Lyon King of Arms, and his sister was the mother of Archbishop Lord Davidson.

As a child Alan Campbell Swinton showed a strong bent towards engineering. An oil painting of him when aged nine, with a steam engine in his hand, was shown at the Royal Scottish Academy Exhibition in 1872, and was labelled prophetically "A Young Engineer." The headmaster of his first school, Cargilfield, Edinburgh, encouraged his mechanical tastes. At this school, although only a boy, he gave exhibitions with a magic lantern and became quite skilled in taking photographs. When only fourteen he took a good photograph of Professor T. H. Huxley, and this, with other portraits, is included in a book called "Autobiographical and other Writings," which was published after his death. In 1878 he was sent to Fettes College, but, as he hated games and at that period took little interest in Latin and Greek, he found the school life uncongenial. He liked, however, to work in the carpenter's shop at Fettes. In 1879, after reading a description of a telephone given in a technical paper, he constructed two telephones which functioned excellently. As the telephone had only been invented some two years previously this would have been a good piece of work for a scientific worker; for a boy of fifteen it was admirable. His house-master, noticing that his scientific absorption interfered with his school work, made him send his telephones home.

In the Easter of 1881 Alan was sent to Havre, where he had lessons in mathematics and French, but he seems to have spent much of his time in taking snap photographs of ships and fishing boats. In this year he visited the Paris Exhibition and was most impressed by the wonderful electrical inventions shown there. In 1882 he was apprenticed to Lord Armstrong in the works at Elswick. During this period he fitted a Chilian battleship with electric gun firing control which enabled any number of guns to be fired simultaneously. He left Elswick in 1887 and set up in London as an electrical contractor and consulting engineer, and installed the electric light in many town and country mansions.

Early in January, 1896, after reading an account in the morning paper of Professor W. C. Röntgen's discovery of X-rays, Swinton was successful in obtaining a shadow photograph by means of a Crookes tube which he happened to possess. A few days later he obtained a shadow photograph of the bones in his own hand. He recognised at once the great benefit of this discovery to mankind. This photograph was reproduced in 'Nature' of January, 1896. He gave many lectures to various societies and did much to spread a general interest in science. I particularly remember hearing him lecture to the Camera Club and the sensation he caused, I think in 1896, by projecting a picture of his own head on the screen when speaking.

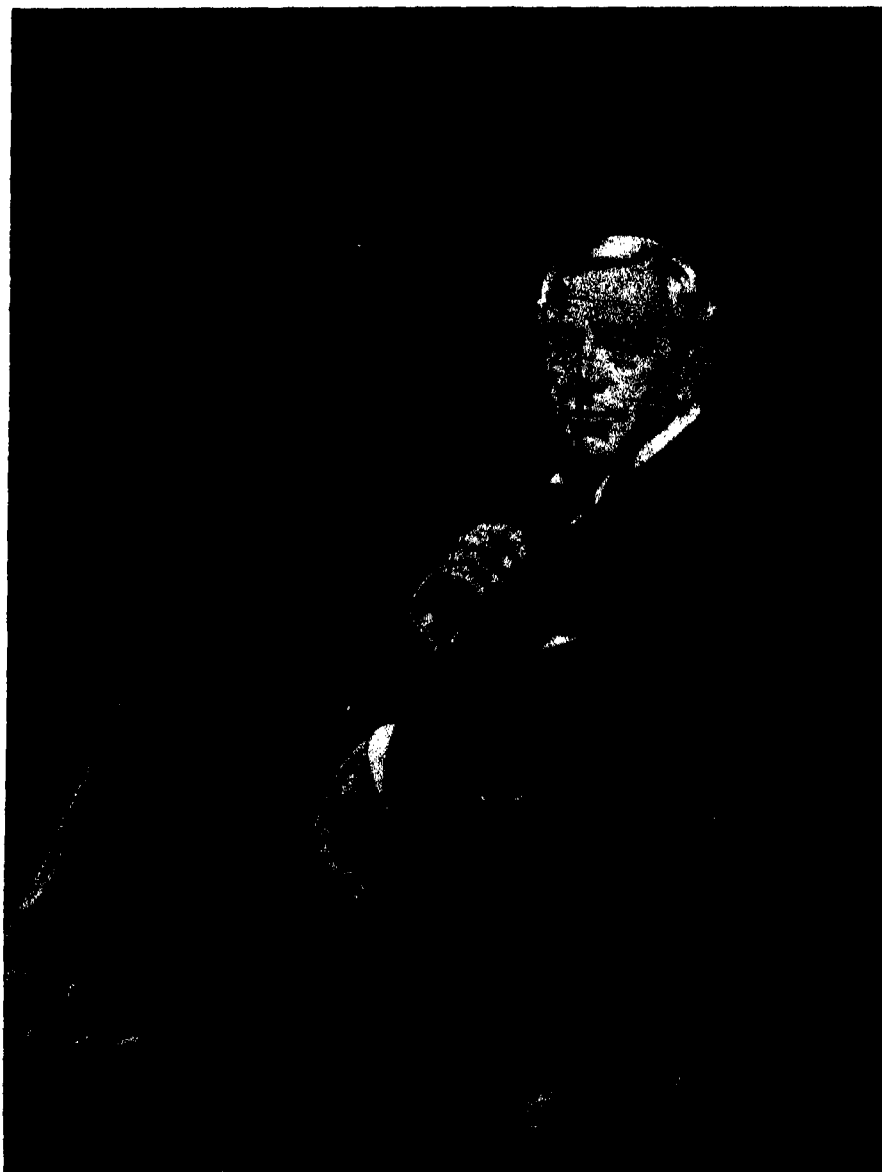
In 1904 Campbell Swinton gave up contracting work and became exclusively a consulting engineer. He was specially interested in radio work. When Marconi came to England, Swinton introduced him to Sir William Preece, and long-distance radio telegraphy soon followed. When listening in 1910 to tests with the Poulsen system Swinton heard articulate speech for the first time. He was associated with the development of the Parsons turbine and was a pioneer of motoring in England. He went out on many of the trials of the pioneer turbine boat, the *Turbinia*, which created a sensation at the Naval Review in 1897 by going at the record speed (at that time) of 33½ knots.

In 1911 he was President of the Röntgen Society and in 1913 of the Radio Society. In 1915 he was elected a Fellow of the Royal Society and served twice on the Council. He had the unusual honour of being Chairman of the Royal Society of Arts for two periods, namely from 1917-19 and from 1920-21, giving four inaugural addresses which were interesting and scholarly. In one of these he prophesied that one day the King would address by word of mouth, and at one and the same time, all the different parts of the British Empire! At the time it seemed a very daring assertion to make.

He was a member of the three professional engineering institutions—the Civils, the Mechanicals and the Electricals. He was a Vice-President of the Electrical Engineers for four years and was an active member of many committees. He was a manager of the Royal Institution and served on the General Board and Executive Committee of the National Physical Laboratory.

For about thirty years Campbell Swinton was a well-known and popular member of the Athenæum Club. He was a bachelor, but entertained his friends at his house in Chester Square. He was proud of having known nearly all the eminent men of science during the last fifty years and liked showing a very interesting collection of their photographs taken by himself.

In 1924 sciagrams taken by his medical adviser proved that his life might be cut short at any minute. He did not, however, let this knowledge interfere with his work or prevent him entertaining his friends as cheerfully as he always had done. The end came on February 19th, 1930.



W. S. W. Linnick,

Mr. Campbell Swinton presented £1,000 to the Society in 1926 to form the nucleus of a general purposes fund. With the help of Sir Charles Parsons and Sir Dugald Clerk he initiated and contributed largely to a fund for the purchase of the freehold of the building in which the Society of Arts holds its meetings. He undertook also to defray the costs of the charter which was recently granted to the British Association.

A. R.

WILLIAM SYMINGTON McCORMICK - 1859-1930.

WILLIAM SYMINGTON McCORMICK was born at Dunbar Terrace, Dumfries, on April 29, 1859. He was the eldest son of William McCormick and Agnes Ann (Symington). His father was in business in Dumfries and was known as a well-read man of good business capacity. His mother was the daughter of the Rev. William Symington, D.D., Minister of the Gospel at Stranraer and Glasgow, and Professor of Divinity in the Reformed Presbyterian Church of Scotland, or Cameronians as they are more commonly named.

McCormick was educated at Dumfries High School, where he does not appear to have shown any particular brilliance, and then at Glasgow University where his powers began to be recognised. His subjects were mathematics and literature, and he acted for a time as assistant to Professor Hugh Blackburn, lecturing on mathematics. After taking his degree at Glasgow in 1880 he went to Germany for the study of literature at the Universities of Göttingen and Marburg. On his return to Glasgow he became assistant to John Nichol, the Professor of Literature. At this time the Scottish Universities were just beginning to open their doors to women, and an institution, Queen Margaret College, was established and was staffed with its own set of lecturers. McCormick was put in charge of the Department of English language and literature.

He also made an experiment in Commerce, joining a Mr. Wilson in a publishing business. This did not come to very much, but it had its influence in helping to give him that detailed knowledge of commerce and its ways which in later life so astonished his friends.

So marked was McCormick's success in Glasgow that he was selected in 1890 to fill the Chair of English Literature in University College, Dundee. He held this appointment for eleven years, acting also as lecturer in literature in the University of St. Andrews. Indeed he was only prevented from succeeding to the Professorship of Literature at St. Andrews by the dissensions between that University and Dundee College, which were then very bitter.

During the part of his life he spent at Glasgow and Dundee McCormick's great qualities became obvious. Professor Nichol, writing at the time of McCormick's application for the Chair at Dundee, said: "It is needless for me to speak of his qualities as a lecturer, in which capacity he has achieved, especially in connection with the University Extension Scheme, a more remarkable success than anyone else of his standing in the West of Scotland. Nor need I dwell on the impression he has made on the minds and the hold he has won over the affections of his pupils. Their enthusiasm on his behalf is the best evidence of his tact and firmness, of his understanding of their difficulties and appreciation of their aspirations, to a degree impossible to any stranger to their antecedents and modes of life." These words might well serve as an indication of those qualities which afterwards in a wider field gave him the unique position which he enjoyed for so long.

During the years of his professorship McCormick was continually engaged on literary work. Perhaps it will suffice here to refer to the part he took in the production of the Globe edition of Chaucer, under the joint editorship of A. W. Pollard, H. Frank Heath and M. H. Liddell. He contributed "*Troilus and Cressida*" and always regarded this work with affection. His literary efforts gradually became centred on Chaucer, on whose works, including the existing manuscripts, he became an authority. This persisted through his life, and in 1926 he spent a holiday at the University of Chicago to study the fine collection of Chaucerian manuscripts which the University possesses. His later work on the critical examination of the texts of Chaucer, which he had nearly finished at the time of his death, is to be published shortly by the Oxford University Press.

McCormick managed to combine his literary work at Dundee with the broader study of University education which finally led him to his commanding position as Chairman of the University Grants Committee. He soon became known to a wide circle as a man whose criticisms and judgment could be trusted; in particular he was invited by the General Medical Council to prepare a report on the entrance examination for the medical profession. In 1901, when Mr. Andrew Carnegie established his Trust for the administration of the £2,000,000 which he set aside for the benefit of the four Scottish Universities and of Scottish students, he invited McCormick to become the first Secretary of the Trust. After very full consideration McCormick accepted this position: this was possibly the most important decision he ever made, for it changed the whole course of his activities. By this time he was a married man, having married Mabel Emily, the daughter of Sir Frederick Cook, Bart., in 1897, and on his appointment as Secretary of the Trust he moved to Edinburgh, living at a house in Douglas Crescent, where he remained till he moved to London in 1920. Both in Edinburgh and later in London he was surrounded by hosts of friends, at first mainly drawn from academic, literary and artistic circles and

later reinforced by members of the Civil Service, and scientific men with whom he became acquainted through the Department of Scientific and Industrial Research.

McCormick's appointment as Secretary of the Carnegie Trust in 1901 opened up a field in which his latent abilities as an administrator had full play. His energy, enthusiasm and breadth of outlook secured to him the immediate support of the distinguished men of affairs who had been nominated as trustees, while his past experience at Glasgow and Dundee gave him a grasp of detail which was never at fault. It is a tribute to his foresight, as testified to by his successor, that the main lines along which the Trust pursues its beneficent activities are still virtually identical with those which he laid down.

Among the influential men with whom McCormick was associated in the early days of the Carnegie Trust was Mr. Haldane, afterwards Lord Haldane. Haldane soon recognised McCormick's exceptional abilities, and when he became a member of the Liberal Government in 1905 was instrumental in getting McCormick appointed a member of the Advisory Committee set up "to advise the Treasury as to the distribution of the grant in aid of colleges furnishing education of a university standard." From 1906 until his death McCormick was intimately connected with all the important steps taken by successive Governments to assist the development of University education. He served on the Departmental Committee appointed in 1907 by the Treasury on the University of Wales and the Welsh University Colleges, and on the Royal Commission (1909 to 1913) on University education in London, which led to the reform of medical education in London, and ultimately to the re-organisation of the University. In the meantime the Treasury Advisory Committee of 1906 had been replaced in 1911 by a new Advisory Committee on University Grants of the Board of Education with much the same terms of reference, and McCormick became its Chairman until 1919, when it was replaced by the present University Grants Committee of the Treasury with the wider terms of reference "to enquire into the financial needs of University Education in the United Kingdom and to advise the Government as to the application of any grants that may be made by Parliament towards meeting them." Since McCormick was Chairman of this new Committee until his death, it may justly be claimed that he was the chief adviser to the Government on the financial needs of Universities for nineteen years.

During the whole of the period from 1906 to 1919 McCormick combined his work in London with that as Secretary of the Carnegie Trust without detriment to either by the simple though fatiguing process of sleeping on the train between Edinburgh and London three or four nights a week. Advancing years, and his added responsibilities as Chairman of the Advisory Council on Scientific and Industrial Research, made this method of saving time continuously more irksome ; but it was not until his duties as Chairman of the University Grants

Committee of 1919 included the survey of Scottish as well as of English and Welsh Universities, that he resigned his position as Secretary of the Carnegie Trust, feeling, as he said in his letter of resignation, "that any attempt on my part to act in the two capacities of Government representative and executive officer of the Trust might lead to misunderstanding and confusion."

McCormick's association with the development of industrial research came about in this way. The Treasury Committee of 1906 was concerned with the development of Arts and the pure Sciences. Higher education in the Applied Sciences was outside their purview, and was comparatively neglected by the State until in 1909 a special department of the Board of Education, under the care of Mr. (later Sir) Frank Heath was created to foster higher education in technology and medicine. It was clearly unwise to attempt to separate the work of the Treasury Committee and of the new department, and it was for this reason that, at the instance of Mr. Runciman, the Treasury Committee was transferred to the Board of Education in 1911. For the next three years McCormick and Heath were working together on a scheme to provide Universities with special funds for the encouragement of research. On the outbreak of war in 1914 it soon became clear that something more was wanted. For many years British Universities had been falling behind those of Germany in the quantity, if not in the quality, of their contribution to scientific knowledge. Neither industry nor the State had shown any marked appreciation of the necessity of encouraging scientific investigation, nor of the value of a trained scientific personnel. There had been, however, a few signs—for instance the modest State support of the National Physical Laboratory, and the establishment of the Advisory Committee for Aeronautics—that there were some public men who appreciated the danger to the State of the neglect of science. Valuable and indeed indispensable as these organisations proved in war time, events soon showed the urgent necessity of expansion in other directions. The extent to which we were dependent on enemy countries for essential materials, the manufacture of which could not be achieved without scientific research on a larger scale, came as a shock to the uninformed, but hardly as a surprise to those who, like the members of the Advisory Committee on University Grants, were fully familiar with the conditions at British Universities. The tentative scheme on which McCormick and Heath had been working assumed a new importance, and during the early part of 1915 a small departmental committee under the chairmanship of Dr. Christopher Addison met almost daily at the Board of Education to work out a comprehensive plan for the encouragement of scientific and industrial research. When the Royal Society sent a deputation to the Government in May, 1915, to urge the case for developing scientific investigation in certain specified directions, and for the establishment of a National Chemical Advisory Committee, the Government was able to announce that machinery to do even more was ready. The Government scheme provided

for the establishment, under the ægis of the Board of Education, of a Committee of the Privy Council for Scientific and Industrial Research with an Advisory Council reporting to the Committee. These bodies were constituted by an Order in Council of July 28, 1915.

Heath was appointed the Secretary of the Advisory Council. McCormick was chosen as Chairman for two reasons : first, to preserve an essential liaison between the new Committee and the University Grants Committee, and secondly for the even better reason that those who knew him, knew he would make a success of it. They were right ; for though his appointment did not pass without criticism in the scientific world, the fears of those who mattered soon disappeared when it was realised how happily and with what effect the new Council worked with their chairman. And indeed in the early days of the movement a scientific chairman might have been handicapped by his own eminence in the world of science ; he might well have been regarded as an expert whose interest in his own studies clouded his judgment. McCormick not only had no axe to grind, but what was even more, no one thought he had an axe to grind.

Events moved rapidly after 1915, and soon the plans of the Council in connection with industrial research were far enough advanced to make it clear that the Board of Education was not altogether an appropriate place for their full development. In the face of some strong opposition, but with the help of McCormick's advocacy and the support of Lord Haldane, it was decided, early in December, 1916, to form a separate Department of Scientific and Industrial Research having Heath as Secretary, and presenting its own estimates to Parliament. This was one of the last acts of Mr. Asquith's Government. An Imperial Trust for the Encouragement of Scientific and Industrial Research was also created at the same time by Royal Charter, and empowered to hold funds and do other things in furtherance of the objects of the Committee of the Privy Council.

To appreciate fully McCormick's work for the Universities and for Science it is necessary to dwell briefly on its peculiar difficulties. As Chairman of the University Grants Committee he had to reconcile the demand of the Universities for freedom in development with the necessity of convincing his Committee, himself and the Government that State funds would be administered wisely and spent judiciously. He had to study the Universities from within ; to criticise as well as to encourage ; to be firm when occasion demanded it ; to strengthen the weak and to guide the strong. The academic world is difficult to handle, but McCormick handled it to perfection. It learned to trust him absolutely ; the affection with which he was regarded and the universal regret with which the news of his death was received were fine tributes to his character. Many people have now forgotten how intense was the suspicion with which the Universities regarded the Government at the time

when McCormick became Chairman of the Advisory Committee on University Grants in 1911; but no one whose knowledge goes back twenty years will regard as an exaggeration the concluding words of the last report of the University Grants Committee—"If the relations between the Universities and the State are now cordial and free from embarrassing suspicions, if a sincere and even jealous regard for the autonomy of the Universities is now an accepted principle of Government policy, this is due to our late Chairman more than to any other man."

Three constructive measures of reform may be quoted as due largely to McCormick's influence and illustrative of his methods and ideals. The first was the establishment of the Federated Universities Superannuation Scheme. McCormick always gave the credit for the broad idea of this scheme to Sir Arthur Rücker in 1912, but there is no doubt that he himself was mainly responsible for its fruition. He seized upon it at once as a constructive suggestion of the first importance, threw himself eagerly into the details, and got it put into operation as from September 29, 1913. Thanks to his energy and stimulating personality the whole scheme was devised and worked out in detail with the full co-operation of the Universities in under one year. After the war he succeeded in persuading the Treasury to give a special grant of £500,000 in order to improve the financial position of older teachers who owing to late entry into the scheme stood to gain little by it. It is a remarkable tribute to the care with which the provisions of the scheme were worked out under McCormick's guidance that not only has it worked admirably and perfectly smoothly for the purpose for which it was originally devised, but has since been applied without change to most of the scientific establishments under Government and to independent organisations such as Industrial Research Associations.

The other University reforms which must be particularly associated with McCormick are those of the Universities of Wales and London. Until recent years these Universities consisted of a number of practically independent bodies each getting financial support from the State through the University Grants Committee. McCormick saw clearly that the continuance of such disorganisation would inevitably lead to one of two evils—either the waste of public money through unnecessary competition between institutions nominally united in a federal band, or a strict control of policy by his own Committee. He refused to depart from the principle of University autonomy; nor would his thrifty Scottish upbringing allow him to turn a blind eye to an avoidable waste of public money. In spite of many difficulties and much opposition he insisted on and finally obtained such a re-organisation of both Universities as to bring the constituent colleges into co-operation instead of competition and to throw on them the collective responsibility of the proper expenditure of public grants. His tenacity is well shown by the fact that it took him fifteen

years to secure the reform of the constitution of London University. He got his way at last ; both Universities are now masters in their own houses, and they owe this mainly to McCormick.

As Chairman of the Advisory Council for Scientific and Industrial Research, McCormick had to contend with difficulties different in kind but no less real. The newer Universities by no means regarded the new Department with enthusiasm ; they feared lest the Council might take away from them more than they gave. Nor was industry at all convinced that a great extension of Government research would be of much assistance to them. But perhaps the greatest problem to be faced was that of overcoming apathy, which is worse than opposition. It was in that respect that McCormick was invaluable. His genuine enthusiasm, his sympathy with other people's difficulties and views, his transparent honesty of purpose found him a way through all difficulties. In the words of a friend he regarded his work for the Department as a mission, not as a job. In early days when the permanent staff was small, he would come to the office every day to talk over current difficulties or future plans. He spent long hours in discussing policy with the members of his Council and with leaders of industry throughout the country. No one could fail to be impressed by his really eloquent pleading for co-operation and combination, nor to respond to his friendly, humorous and yet firm way of managing a meeting. It was after a visit to Lancashire to meet the leaders of the cotton industry that he came back convinced of the need for a Government fund from which grants could be made to encourage co-operative research by industry. " You send me to preach the Gospel to hungry men," he told the Lord President and the Chancellor of the Exchequer, " with a Bible in one hand but no bread in the other." Within twenty minutes he persuaded Mr. McKenna to obtain a million sterling for the Department to be spent in grants to co-operative Research Associations.

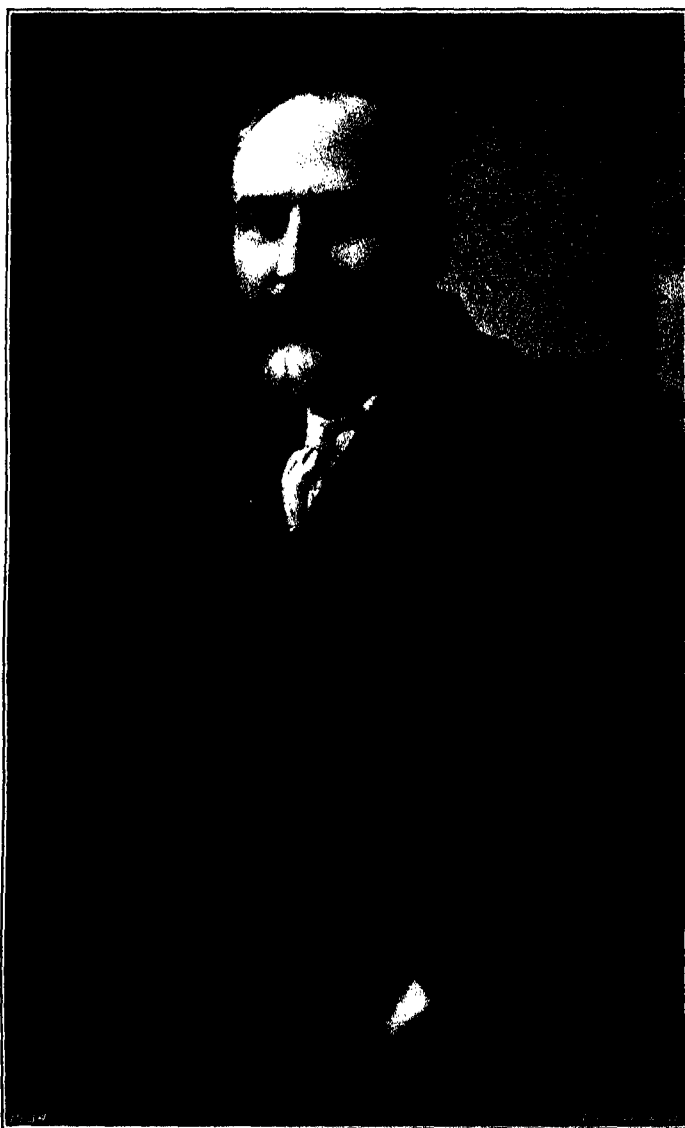
As the Department grew and became more firmly established, McCormick's long informal talks inevitably became rarer, but he was always available for consultation, and his knowledge of men, his native caution and wisdom, made his advice invaluable. He lived to see the Department grow within fifteen years from small beginnings to an organisation controlling an annual expenditure of over £700,000 in large national research establishments and in the encouragement of research in Universities and by industry ; to see growing up a spirit of friendly co-operation on all sides, and the apathy on the part of public men replaced by a profound, and not always entirely justified, faith in the value of scientific research as a cure for national ills. His work for science was done before he died, as well and as thoroughly as any man's work was ever done. It was recognised, to his surprise and deep gratification, by the highest honour which it is within the power of the scientific world to bestow, when in 1928 the Council of the Royal Society recommended him for election

to the Society as a person who "in their opinion had rendered conspicuous service to the cause of science."

A brief reference must also be made to McCormick's work in connection with the Carnegie United Kingdom Trust, which was formed in 1913. He was an original Trustee and Chairman of its Music Committee which undertook the publication of the great Tudor and Elizabethan Church Music, instituted a scheme for publishing the work of modern British composers, and gave much needed assistance to the Musical Competition Festivals and to the "Old Vic." He also took an active part, as a member of its Library Committee, in the development of the Rural Library movement, the formation of the Central Library for Students and of the School for Librarians at University College, London. He moved finally from his home in Edinburgh to Farnham, Hampstead, in 1921. He remained a member of the Executive Committee of the Carnegie United Kingdom Trust for a while, and although he was no longer able to take so active a part in its work, he found an outlet for his interest in music and the drama by becoming Chairman of the British National Opera Company, and a member of the Committee of Management of the "Old Vic." He was knighted in 1911, and created G.B.E. in 1929.

In person he had a crumpled, humorous face, with locks of silver hair falling over his forehead. Vivacious in conversation, his expressive eyes seemed to pass in a flash from one mood to another. A robust, vigorous man in his youth, he was handicapped in later years by some ill-health, but momentary fits of depression caused by physical pain or the unexpected refractoriness of human nature were soon chased away by his strong sense of humour. Fortunately his features and handsome presence are preserved for future generations in a fine portrait of him by his close friend Sir William Orpen, which hangs in the Tate Gallery and is reproduced here by permission of the Trustees.

He liked talking better than writing. He gesticulated freely when he talked, had a loud, infectious laugh, and loved a good joke or story. He was apt to be discursive when he did not know his audience well, and in the process of feeling their reactions to his arguments he would "wind into his subject like a serpent." But if he loved talking, he was also prepared to listen. He listened to everyone, never obtruding advice except when it was sought, and acting always on the assumption that those he had to deal with were reasonable people if taken in the right way. The universal appeal which his nobility of character and soundness of judgment made to others was perhaps the chief cause of his success as an administrator, and the outward sign of his greatness as a man. No one surely ever had a wider circle of intimate affectionate friends, and for several very good reasons. Endowed himself with a most affectionate nature, he unconsciously rated his friends above their merits and let them see at a very early stage of friendship that he took a real interest in their ambitions, their joys, and their sorrows, and all with a vast experience of



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J. O. Arnold.

life behind it. He found delight and recreation in the company of his friends, and to "sit next to Mac" became a cherished privilege in many circles.

In the early part of last year he was engaged on a strenuous round of visits to Universities, which was not quite finished when he started in March on a voyage to the Mediterranean in the hopes of regaining his strength for the remainder of his task. The rest and freedom from worry seemed to be doing him good, but he died suddenly in his sleep on the morning of March 22, 1930.

R. T.

H. T. T.

JOHN OLIVER ARNOLD—1858–1930.

PROFESSOR J. O. ARNOLD, whose death occurred at Oxford on March 27 last, was born at Peterborough on December 29, 1858, the son of Mr. David Nelson Arnold, general manager of the Midland Railway Carriage and Wagon Company. He was educated at King Edward VI's Grammar School, Birmingham, and entered the Navy as a cadet on H.M.S. "Conway," making a journey to India in that capacity, but shortly afterwards leaving to take up metallurgy as a profession. Although his naval career was a short one, he never lost his love for the sea, and he remained all his life a keen yachtsman, although the restrictions of the war years forced him to leave the Western coasts and confine himself to the waters of Windermere, on the shores of which he ultimately settled after his retirement.

At the age of twenty he entered the engineering department of Messrs. Brown, Bayley & Dixon, and later held appointments, first with the Farnley Iron Company, Leeds, and then in the Spanish Steel Works, Sheffield, combining with the latter appointment a consulting practice as a metallurgist.

In spite of the great importance of the steel industry to Sheffield, there existed no means of providing training for chemists and metallurgists in the city before 1883, although occasional courses of lectures were given by visiting lecturers. In that year, Dr. W. M. Hicks having been appointed Principal of the Firth College, it was decided to make provision for systematic training, and W. H. Greenwood was appointed as Professor of Engineering and Metallurgy. This step was taken largely on the recommendation of Dr. H. C. Sorby, to whom we owe the foundation of metallography as one among many of his original contributions to science. In 1886 new buildings for the Technical

School were opened, but the results were for some time disappointing. When Professor Greenwood retired in order to return to industry, Arnold was invited to deliver the lectures in metallurgy, while still continuing his consulting practice. He has recorded his surprise, on entering the large lecture room for the first time, on finding that the audience consisted of one student. Shortly afterwards he was appointed full-time Professor, but the chairman of the governing body remarked that as the salary, £250, was a huge one for a young man, he must understand that if by the end of the first session the department had not been made a success, the appointment would come to an end. Success was, however, never in doubt. Arnold's teaching, bringing science into direct touch with the industry from which his students came, made an immediate appeal, and the number of students grew rapidly. By 1890 he had so far persuaded the authorities of the value of his methods that he was enabled to erect a small-scale steel works, the equipment of which included a 25-cwt. Siemens furnace and a pair of Huntsman crucible furnaces. The object of this new departure in metallurgical education was by no means to make experience in the works unnecessary, but to give the students such an insight into the processes of manufacture as to help them to attack the problems of industry with understanding, whilst at the same time enabling them to acquire a certain degree of manual skill. This was also encouraged by the very thorough drill in quantitative analysis on which he insisted in the laboratory. Twelve years later this small plant was replaced by a larger building on an island site, equipped with a Siemens furnace of 2-tons capacity and other furnaces and forging appliances. This plant has proved to have great value for the purposes of research as well as of instruction.

In 1897 the Firth College, the Medical School, and the Technical School were united to form University College, Sheffield, and in 1905 the institution attained the rank of an independent University. A few years later separate degrees of Bachelor, Master and Doctor of Metallurgy were instituted, and in 1917 a Faculty of Metallurgy was established, with Arnold as its first Dean. At the end of 1919, after a period of absence through ill-health, he felt himself compelled to resign his chair, and lived in retirement, first in London and then at Bowness-on-Windermere. The University recognised his great services by appointing him Emeritus-Professor. He married, in 1883, a daughter of the Rev. James England, of Liverpool, and had two sons and a daughter. Mrs. Arnold is well known as a novelist.

Arnold's chief claim to remembrance rests on his work in the application of scientific knowledge to the manufacture and use of steel. As far back as 1863, Sorby had applied the microscope to the study of steel, and had succeeded in identifying the principal constituents, but his work attracted little attention until the independent studies of Adolf Martens in Charlottenburg from 1878 onwards brought about a general interest in metallographic methods. The early

work of Martens was much less accurate than that of Sorby, but it attracted others, and in a few years great progress was made. Arnold eagerly adopted the methods of his friend Sorby, and was the means of persuading industrialists that the microscope could give information of real value for the control of manufacture and the detection of the causes of failure. For some years he placed little trust in photographic methods of recording structure, in spite of the beautiful results obtained by Sorby, and his papers were long illustrated by reproductions of drawings by members of his staff, some of which show the most minute detail, evidence of remarkable skill and patience. In his later papers he made full use of photo-micrography. He also developed the determination of cooling curves, preferring the "inverse-rate" method of plotting to any other, and making important improvements in the experimental methods. Essentially a chemist, he devoted much attention to analytical processes, and his only publication in book form is his "Steel Works Analysis," first published in 1891, and in its later editions revised by Dr. F. Ibbotson. Not only did he improve existing methods of analysis of steels and devise new ones, but the presentation of the subject by the two authors provides an admirable application of advanced inorganic chemistry to practical purposes, a theoretical understanding of the complex reactions involved in certain of the estimations being essential to their accurate performance.

In 1894 Arnold published the first of a series of papers on the carbides contained in steels, describing investigations which he carried on for many years with Professor A. A. Read, of Cardiff. The carbide of iron, Fe_3C , known as cementite, had been discovered by Sir Frederick Abel in 1885. It was now isolated by a method of electrolytic dissolution, first applied to cast iron by Binks and Weyl, and it was shown for the first time that the bright laminae in pearlite were identical with free cementite, pearlite being thus an intimate intergrowth of ferrite and cementite. In subsequent papers the method was extended to steels containing other metals, such as chromium, manganese, nickel, molybdenum, and cobalt, and formulæ were deduced for the simple and complex carbides contained in them. Although the method of isolation by chemical means is not free from objection, so that some of the products are not now recognised as definite compounds, these investigations were of the greatest value in providing a first survey of the constitution of complex steels, especially as the analyses were made on alloys prepared with great care, and were always accompanied by mechanical and physical tests.

In 1895 a paper contributed to the Institution of Civil Engineers opened a controversy which lasted for many years, and raged among the metallurgists of Europe with remarkable intensity. Floris Osmond had described in 1890 the existence of two modifications of iron, stable within different ranges of temperature, α -iron being the stable form below 700°C. , and β -iron that stable above 855° , the transformation of one modification into the other occurring at different

temperatures between those limits according to the conditions. It was Osmond's view that the hardness of quenched steel was due to the great intrinsic hardness of β -iron, which changed into the soft α -modification on cooling, but could be retained on rapid cooling if carbon were present, the temperature of the change being lower, the higher the proportion of carbon. Osmond also showed quite clearly the influence of other metals on this change. Arnold, on the other hand, attributed the hardness of quenched steel entirely to the formation of a compound of iron and carbon at high temperatures, dissociating on slow cooling but being capable of retention on quenching. The maximum hardness being obtained with 0.89 per cent. of carbon, he assigned to this glass-hard compound the formula Fe_{24}C , breaking up on cooling into free α -iron and cementite, Fe_3C . He pointed out, with great cogency, that pure iron could not be hardened by quenching, and that the production of hardness depended always on the presence of carbon. The controversy between the supporters of the "allotropic" and the "sub-carbide" hypotheses of hardening was long and even heated, and neither side gained a complete victory, since the modern view involves both allotropy and the influence of carbon. The hardness of β -iron was abandoned and new allotropic modifications of iron were added to the original two, being named γ -iron (above 900°) and δ -iron (above 1400°). Of these, only γ -iron has the property of taking up considerable quantities of carbon into solid solution, and the retention of metastable products of the partial decomposition of that solution on quenching is recognised as the cause of the increased hardness, although the exact mechanism of hardening is complex and even yet subject to differences of opinion. However, it was Arnold's insistence on the chemical and mechanical properties of iron and steel, combined with his thorough knowledge of their behaviour in the workshop, that led him to reject, perhaps rather scornfully, views which appeared to him to be based only on hypothetical reasoning. In any case, the discussion was extraordinarily productive of research, and the attention of able chemists was drawn to the subject, thus leading to many important discoveries in connection with steel.

Always individualistic in his outlook, Arnold did not welcome the introduction of the language of physical chemistry into metallurgy, and always continued to use his own nomenclature, so that the reader is sometimes obliged to translate his descriptions of structure into the form generally adopted by metallurgists. Disliking the use of personal names in the description of micrographic constituents, he rejected such names as "troostite," "martensite," or "austenite," preferring to speak of "emulsified carbide" and to use similar descriptive terms.

It is natural that, as the head of the metallurgical school in Sheffield, Arnold's interest should have been mainly in the finer qualities of steel. He always regarded shear and crucible steels, made from the purest Swedish raw materials

and converted in the traditional manner, as representing the best practice, and although he interested himself in the advance of the newer processes, these represented the standard by which all other steels had to be judged. He was an ardent champion of the maintenance of high quality, and could always be counted on to defend the local industry against attempts to gain trade by supplying inferior products in substitution for the genuine steel, as in the cutlery industry, to which he rendered great services, earning the confidence and gratitude of the workmen. His experiments, carried out in collaboration with Dr. W. Ripper of the Engineering Department, on high-speed tool steels, did much to establish that important branch of manufacture. In 1889 Mr. A. F. Wiener, an Austrian, brought the metal vanadium to his notice, and Arnold's experiments proved that great advantages were gained by the addition of that metal to tool steels, this step leading to the production of tools of much greater efficiency than had been available before. In later years he also took a share in the introduction of molybdenum as an alloying metal.

It was as a teacher that Arnold exerted the greatest influence. He was an admirable lecturer, clear and fluent, with a fine voice and a vigour and picturesqueness of language that delighted his hearers, and made his intervention in discussions an event greatly enjoyed by members of the Iron and Steel Institute and other technical bodies. He had a reputation for pugnacity, but he was liked best by those who knew him best. His students, to whose interests he devoted himself whole-heartedly, held him in great affection, in no way diminished when, as sometimes happened, they came in later years to hold opinions on metallurgical questions opposed to his. In him metallurgy loses one of its outstanding figures, a man of genial personality, sterling honesty, and great force of character, who did much to raise the standard both of the science and of the industry which depends on it.

Professor Arnold was elected a Fellow of the Royal Society in 1912. He was awarded the Bessemer Medal of the Iron and Steel Institute in 1905, and in 1925 was appointed an Honorary Vice-President of that body.

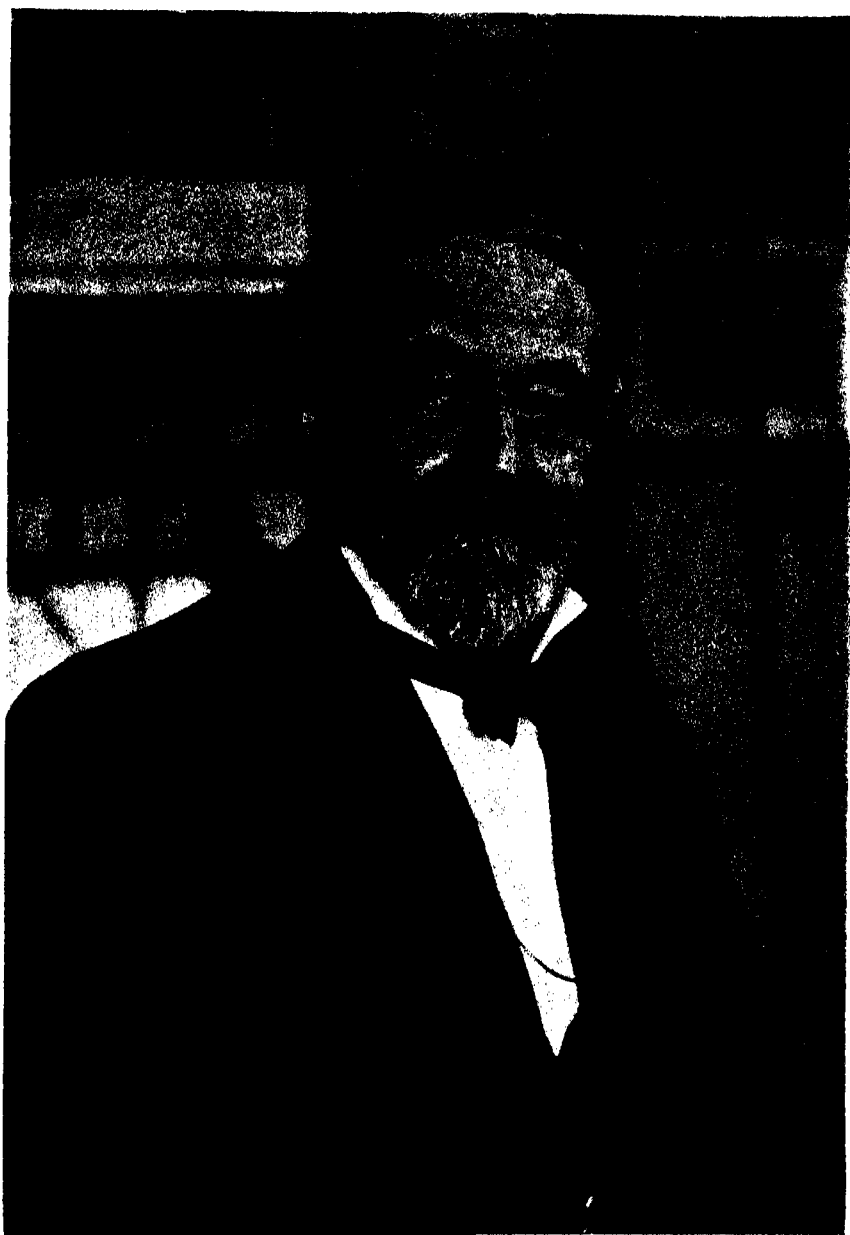
C. H. D.

JOSEPH ACHILLE LE BEL—1847–1930.

THE death of JOSEPH ACHILLE LE BEL, which occurred in Paris on August 6, removes a veteran who had been closely associated with the rapid development of organic chemistry during the latter part of the last century. Le Bel was born at Pechelbronn, Alsace, on January 21, 1847, and was a nephew of Boussingault, the agricultural chemist. He was a student at the École Polytechnique from 1865 to 1867 and became successively assistant to Balard, the discoverer of bromine, at the Collège de France, and to Würtz, at the École de Médecine, in Paris. For some time he was in charge of the petroleum workings at Pechelbronn, in which his uncle was interested; he became and remained an ardent partisan of Mendeléeff's view that the petroleum deposits result from the action of steam on metallic carbides at volcanic temperatures.

Le Bel holds an honoured position in the history of science as one of those eminent French natural philosophers who discovered and worked out the earlier consequences of optical rotatory power. Arago observed in 1811 that the plane of polarisation of a beam of polarised light is deflected by passage through a plate of quartz cut perpendicular to the optic axis; in 1815 Biot found that certain organic liquids, such as turpentine, are also optically active in the same sense. In the 'fifties and 'sixties, Pasteur concluded from his classical investigation of the tartaric acids that the optical rotatory power of aqueous solutions of these organic compounds arises from asymmetry of their molecular configurations. No progress was made, however, in the problem of ascertaining the definite arrangement in three-dimensional space of the atomic components of optically active molecules, called for by Pasteur's fundamental conclusion, until the doctrine of the asymmetric carbon atom was enunciated.

The theory of the asymmetric carbon atom was put forward independently and practically simultaneously by van 't Hoff and Le Bel in 1874; after a brief period of discussion, accompanied by a certain amount of lively ridicule, the theory became universally accepted and to-day forms the foundation of the vast subject of the stereo-chemistry of carbon compounds. The theory was evolved in a somewhat different fashion by its two authors. Van 't Hoff proceeded from the assumption that, in such a molecule as that of methane, CH_4 , the four valency directions of the carbon atom are directed from a centre, representing the carbon atom, towards the apices of a regular circumscribing tetrahedron, the four hydrogen atoms being centred at those apices. In the substitution derivatives of methane of the types, CX_3Y , CX_2YZ , X , Y and Z being univalent radicles, no isomerism should exist if the four radicles lie at the apices of the tetrahedron as foreshadowed by the theory; when all four radicles attached to the central carbon are different, as in the type CWXYZ ,



Y. M. L. Bell

two isomerides should exist, the space configuration of one being the mirror image of that of the other. A carbon atom so attached to four different radicles is termed asymmetric, and, in accordance with the conclusion of van 't Hoff and Le Bel, all substances which contain one asymmetric carbon atom in the molecule have been found to exist in two mirror-image, or enantiomorphously related, configurations, of arithmetically equal but algebraically opposite rotatory powers.

Le Bel arrived at the theory in a somewhat different manner. He discussed the mode in which the four univalent radicles attached to a quadrivalent carbon should arrange themselves as a pure question of equilibrium, and hence arrived at the tetrahedral environment of the central carbon atom with the same consequences, as regards asymmetry, as those of van 't Hoff. It is not yet settled whether van 't Hoff's view, that the carbon atom carried four valency directions directed towards the four apices of a circumscribed regular tetrahedron, is preferable to that of Le Bel, but the tendency of modern organic chemistry is certainly towards the Le Bel implication that the four carbon valency directions are not so fixed. Probably, however, both men were making in 1874 an incomplete statement of the same thing; although more than half a century has elapsed, it is not yet possible to state the theory of the asymmetric carbon atom in more definite and explicit terms than was done at that date.

Le Bel was the first to separate an optically active component from the synthetic mixture of the two mirror-image components of a compound containing an asymmetric carbon atom; he did this in most cases by taking advantage of the selective destructive action of lower organisms on the laevo- and dextro-isomerides. He was also the first to show that when the asymmetric carbon atom of an optically active substance of the type, CWXYZ, becomes symmetric by conversion into the allied compound, CX₂YZ, the optical activity disappears.

Later, Le Bel extended his stereochemical conceptions to quinquivalent nitrogen compounds and announced in 1891 that he had been able to obtain optically active methylethylpropylisobutylammonium salts; this observation could not be confirmed by others, and is no doubt mistaken. The laboratory technique for dealing with such complex substances had not then been sufficiently worked out, and it was not until 1899 that the first optically active substituted ammonium salts containing an asymmetric quinquivalent nitrogen atom, but no asymmetric carbon atom, were first prepared.

Le Bel did not publish a great amount of experimental work, probably because he held no academic post and so found few collaborators; his writings cover, however, a wide range of subjects and are permeated by a quite uncommon philosophic spirit. He was an individualist and mixed little with his scientific colleagues; he was intolerant of officialdom in any of its aspects,

and was wont to express his contempt of bureaucracy with some vigour. His originality of thought, his outspokenness, and his unconventionality, indeed bohemianism, made him somewhat difficult of access, but in congenial society he was a delightful companion, full of knowledge of the world and sparkling with anecdote and caustic wit. He maintained his interest in science to the end, and, so late as April last, offered a money prize for the rediscovery of a microscopic green alga, found and lost by him, which had the power of converting atmospheric nitrogen into ammonia.

Le Bel was president of the French Chemical Society in 1892; he was a Commander of the Legion of Honour and a member of the Paris Academy of Sciences. He was elected an honorary fellow of the Chemical Society in 1908 and a foreign member of the Royal Society in 1911; in 1893 both he and van 't Hoff became Davy medallists of the Royal Society. In 1925 he made a gift of money to the Society with the request "that you subsidise research rather than subsidise students, for I think we have plenty and to spare of savants who have fattened on examinations, but not enough of the people who employ their time in solving problems of interest. Hitherto the Royal Society seems to me to have used its money well. I hope that it will continue." He bequeathed the whole of his estate to the French Chemical Society.

W. J. P.

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